The adsorption and elution of Pt-, Pd- and Au cyanide using activated carbon

by

Cornelius Albert Snyders

Dissertation presented for the Degree

of

DOCTOR OF PHILOSOPHY

(Extractive Metallurgical Engineering)

in the Faculty of Engineering

at Stellenbosch University

Supervisor

Prof. Steven Bradshaw

Co-Supervisor

Prof. Guven Akdogan

March 2015

Declaration

By submitting this dissertation electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: 17 February 2015

Abstract

In order to exploit lower grade and complex platinum group metal resources, cheaper and more efficient alternatives to the conventional mill-float-smelt-refine route are being sought. Leaching of platinum and palladium with cyanide has been proposed a number of times as a promising precious group metals (PGM) process option, and although platinum extractions are problematic, progress into the understanding of cyanide leaching of PGM containing ore and concentrate has been made. The platinum and palladium leaching will typically take place at elevated temperatures, which can range from 55°C on heaps to 180°C in autoclaves, with a better degree of leaching occurring with higher temperatures. Although this process for Pt and Pd extraction is a promising process option, research regarding the feasibility of the subsequent upgrading and recovery of the pregnant PGM leach solution, however, has been lacking. Since the carrier-phase extraction of gold using activated carbon offers significant advantages over other processes in terms of simplicity, the high pre-concentration factor, rapid phase separation, and relatively low capital and operating costs, activated carbon was deemed the most suitable sorbent for a Pt and Pd adsorption and stripping process.

Very little is published on the adsorption of PGM cyanides onto activated carbon and when the effect of impurities such as base metals and thiocyanate together with a suitable elution method, are considered, no information could be found in the open literature. This study was launched and in general it was found that the activated carbon process does seem to be a viable process consideration for the upgrading of PGMs in a cyanide leach stream. Adsorption rates for dilute PGM solutions (0.15mg/L Pt, 0.38 mg/L Pd, 0.1 mg/L Au) in a stirred vessel indicated a high rate of adsorption within the first 60 minutes (giving more than 98% recovery of precious metals). A comparison of the Pt isotherm (25°C) to Au isotherms from literature indicated a similar loading capacity, while that of Pd was found to be significantly lower. In common with most diffusion controlled processes, an increase in the adsorption rate of platinum, palladium and gold cyanide with an increase in temperature was observed, while experiments with consecutive contacts of the PGM cyanide solution onto the activated carbon revealed that with an increase in temperature, the amount of PGMs that were adsorbed, decreased with each loading. In the absence of free cyanide and base metals, it was found that after 4 consecutive contacts, 99% of the total amount of platinum and palladium adsorbed at 25°C, compared to 85% of the platinum and 83% of the palladium at 50°C. No difference could be seen between the adsorption of gold cyanide at 25 and 50°C after 4 contacts. It has also been established that the detrimental effect of free cyanide on the adsorption of PGMs will increase as the temperature increases. The detrimental effect of the presence of Cu and Ni was found to depend on the amount of these base metals adsorbed, which in turn will depend on the cyanide concentration and the solution temperature. Adsorption of Pt and Pd has been found to be significantly more affected by temperature, cyanide and base metals than the adsorption of gold and needs to be carefully taken into consideration with the design of a PGM adsorption circuit to ensure sufficient Pt and Pd recovery. It is therefore highly likely that an

activated carbon recovery process for Pt and Pd cyanide will not be as robust as the gold CIS (carbon-in-solution) process, which is considered to be one of its main advantages.

The feasibility of eluting platinum and palladium cyanide complexes from activated carbon was investigated. It was found that platinum and palladium elute from activated carbon almost to completion in 4 to 5 bed volumes (BV) at 80°C, while the elution of gold at this temperature is slow, with a significant amount of gold (≈ 55 %) still to be eluted after 16 bed volumes. An increase in Pt and Pd elution kinetics was demonstrated with an increase in temperature with 99% recovery achieved at 4 BVs with an elution temperature of 95°C.

Cyanide pre-treatment has been found to have a large influence on PGM elution. The effect of the NaCN concentration shows an increase in the recovery of Pt, Pd and Au as the cyanide increases from 0 to 2 %, after which the recovery starts decreasing again as the NaCN concentration increases from 2 to 4%. The NaOH concentration was also found to affect the PGM recovery and at 0% NaCN, an increase in the recovery is seen, while at a higher cyanide concentration (2 and 3% NaCN) a decrease in the PGM recovery occurs when the NaOH concentration is increased from 0.22% to 1.65%.

A general decrease in Pt, Pd and Au recovery was seen as the ionic strength of the elution water increased and is consistent with literature on Au elution.

The effect of a hydrochloric acid pre-treatment, which forms part of the process to remove calcium build-up from the activated carbon, was investigated, and for all the cases the Pt and Pd recovery increased when an acid pre-treatment was performed, compared to no acid pre-treatment. In none of the cases did any of the Pt, Pd or Au elute with the acid or the following rinsing water. The acid pre-treatment performed at 70°C removed a significant 64% to 75% of the Ni present and an additional 9.1% to 10.5% in the following rinsing water step.

In the presence of copper cyanide, the elution order has been found to be copper, palladium, platinum and gold, which is the opposite order of adsorption preference. The cyanide pre-treatment has also been found to have a major influence on the elution of Cu and can be explained by the difference in the absorbance strength between the different copper cyanide complexes. The presence of Cu did not have a negative effect on the elution of the PGMs at strong pre-treatment (2% NaCN and 0.55% NaOH) conditions, but at weak pre-treatment conditions (0% NaCN) the recovery of Pt and Pd was reduced by between 10 and 18% after 5 BVs when Cu was present.

The presence of 100 mg/L KSCN salt added to the leach solution during the adsorption stage, reduces the elution recovery of the PGMs at 4 BVs from 90% for Pt and Pd, when not present, to approximately 70% when present. The addition of the additional K^+ ions reduced the recovery by less that 4% at 4 BV, which indicates that the possible formation of a PGM bonding with thiocyanate ($[Pt(SCN)_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$), which adsorb onto carbon, but doesn't adsorb with water, cannot be ruled out completely.

A maximum amount of 0.15% for Pt, 0.28% Pd and 0.6% Au was found to report to the pre-treatment solution at 25°C. For higher pre-treatment temperatures, the amount of Pt and Pd reporting to the pre-treatment solution increased significantly to approximately 8% at 80°C, while the increase in gold was marginal to 0.8% at 80°C. For the higher loading on the activated carbon (7000 mg/kg Pt and Pd), which is expected to be a better representation of plant conditions, 0.07% Pt, 0.11% Pd and 0.12% Au reported to the pre-treatment solution. The PGMs reporting to the pre-treatment solution is attributed to the distribution of the PGMs on the carbon particle, and even though very small, a certain amount of these PGMs would readily desorb or wash off the carbon.

It has thus been established here that the stripping of adsorbed platinum cyanide complexes from activated carbon consists of a two step batch process, which involves the pre-treatment of the metal-loaded activated carbon with a relatively strong sodium cyanide and sodium hydroxide solution, prior to the elution step with de-ionized water at 80°C. Through the development of a mathematical model to describe this process, it was found that the rate of release of the platinum ions is governed by the amount of platinum and sodium on the activated carbon and the concentrations of these ions in the bulk of the liquid. This is mathematically described by a modified Freundlich isotherm equation and the mass transfer diffusion equation. The dependency of the platinum elution rate on the sodium concentration on the activated carbon, as suggested by gold related literature (Van Der Merwe and Van Deventer, 1990, Stange, 1990), is confirmed. Furthermore it has been found that the rate of platinum elution interchangeably depends on the equilibrium of the Pt ions at the carbon-liquid interface and the mass transfer of these Pt ions from the interface to the bulk liquid. As both of these rate-limiting factors were found to depend on the sodium concentration, the dominant platinum elution rate limiting factor shifts as the sodium concentrations change as the elution progresses. Four main time periods are used to simplify and to describe this process. The benefits of fundamentally understanding this process can ultimately lead to improved elution, better process control, shorter elution times, smaller elution columns or assist in the development of a continuous elution process.

Samevatting

Nuwe prosesse om komplekse laer graad waardevolle metaal ertse te onwikkel in plaas van die konventionele maal-flotasie-smelt-raffineer proses word tans ondersoek. Loging van platinum en palladium met sianied is verskeie kere al voorgestel as n belowende proses opsie en alhoewel die ekstraksie van platinum nog n probleem is, is vordering al gemaak om die logings proses beter te verstaan. Die loging van platinum en palladium met sianied sal tipies plaasvind by hoër temperature wat kan wissel van 55°C in n hoop logins proses tot 180°C onder druk. Beter loging vind plaas soos wat die temperatuur styg. Alhoewel hierdie proses belowend is, is daar nog geen navorsing beskikbaar t.o.v die volgende stap in die proses wat die opgradering van die logings oplossing behels. Aangesien die gebruik van geaktiveerde koolstof in die goud industrie baie voordele inhou soos die eenvoudigheid van die proses, hoë opgraderings faktor, relatiewe vinnige adsorpsie en lae kapitaal en operationele kostes, mag hierdie tegnologie ook geskik wees vir Pt en Pd.

Baie min is gepubliseer oor die adsorpsie van waardevolle metale (PGMs) met geaktiveerde koolstof en wanneer die effek van onsuiwerhede soos basis metale en thiosianied saam met n afstropings metode in ag geneem word, kon geen informasie in the literatuur gvind word nie. Hierdie studie is dus geloots en in die algemeen is daar bevind dat die geaktiveerde koolstof metode wel n geskikte oplossing bied vir die opgradering van PGMs in n sianied logings stroom. Adsorpsie snelheid vir verdunde PGM oplossings (0.15mg/L Pt, 0.38 mg/L Pd, 0.1 mg/L Au) in bekers wat geroer is, was vinnig vir die eerste 60 minutte (98% herwinning van die PGMs) en n vergelyking tussen die Pt adsorpsie isoterm en gepubliseerde Au isoterms wys op n relatiewe soorgelyke ladings kapasiteit. Die isotherm van Pd was egter laer. Soortgelyk aan meeste diffusie beheerde prosesse, het n verhoging van temperatuur gelei tot vinniger adsorpsie snelhede vir Pt, Pd en Au. Indien oplossings egter herhaaldelik met dieselfde koolstof in kontak gebring word, is bevind dat met n verhoging in temperatuur, die totale hoeveelheid PGMs wat absorbeer, met elke kontak verminder. In die afwesigheid van sianied en enige basis metale, het die totale hoeveelheid Pt en Pd wat geabsobeer is na 4 opeenvolgende kontake verminder van 99% by 25°C tot 85% adsorpsie van Pt en 83% Pd by 50°C. Daar was geen veskil tussen die adsorpsie van Au by 25°C en 50°C na 4 kontakte nie. Dit is ook vasgestel dat die negatiewe effek van vrye sianied in die oplossing, groter word soos wat die temperatuur verhoog. Die negatiewe effek van die teenwoordigheid van Cu en Ni, hang af van die hoeveelheid van hierdie metale wat absorbeer word wat weer bepaal word deur die sianied konsentrasie asook die temperatuur van die oplossing. Die mate waar in Pt en Pd ge-absorbeer word deur koolstof, word aansienlik meer beinvloed deur temperatuur, sianied konsentrasie en die teenwoordigheid van basis metale as wat die adsorpsie van Au beinvloed word. Met die ontwerp van n PGM adsorpsie proses, sal dit sterk in aanmerking geneem moet word, om seker te maak dat so min as moontlik Pt en Pd verlore gaan. Dit wys ook dat n geaktiveerde koolstof proses vir Pt en Pd, nie so onvatbaar vir proses veranderings sal wees soos wat die Au proses is nie, wat as een van die groot voordele van die Au proses beskou word.

Die afstropery van die Pt en Pd sianied komplekse is ondersoek en gevind dat by 80°C, amper al die Pt en Pd binne 4 to 5 bed volumes (BV) van die geaktiveerde koolstof gestroop kan word. Die afstropery van Au by hierdie temperatuur is stadig en sowat 55% van die Au bly nog oor op die koolstof na 16 BVs. Die snelheid waarteen die Pt en Pd afgestroop word verhoog indien die temperatuur verhoog word en by 95°C is 99% van die Pt en Pd herwin na 4 BVs.

Voorafbehandeling van die gelaaide koolstof met sianied, het n groot uitwerking op die PGM afstroping. Soos wat die NaCN konsentrasie verhoog word vanaf 0 tot by 2%, verhoog die PGM herwinning maar daal ook weer indien die NaCN konsentrasie verder verhoog word vanaf 2% tot by 4%. Die NaOH konsentrasie het ook n invloed gehad. By 0% NaCN, het die PGM herwinning verhoog soos wat die NaOH konsentrasie verhoog is maar by hoër sianied konstrasies van 2 en 3%, is n daling in die herwinning waargeneem soos wat die NaOH verhoog is vanaf 0.22% tot by 1.65%.

N algemene daling in die Pt, Pd and Au herwinning is waargeneem soos wat die ioniese sterkte van die stropings water toegeneem het. Dit stem ooreen met gepubliseerde navorsing oor die afstroping van Au.

Om kalsium van die geaktiveerde koolstof te verwyder, word die koolstof vooraf met soutsuur gewas. Hierdie stap is vir Pt en Pd ondersoek en daar is bevind dat vir al die gevalle, die herwinning hoër was wanneer die gelaaide koolstof met soutsuur behandel is teenoor geen behandeling nie. In geen van die gevalle, is Pt, Pd of Au saam met die soutsuur of die daaropvolgende was water afgestroop nie. Voorafbehandeling met soutsuur teen 70°C lei wel daartoe dat tussen 64 en 75% Ni afgestroop word saam met die soutsuur en n verdere 9.1 to 10.5% saam met die daaropvolgende was water.

In die teenwoordigheid van koper sianied, word Cu eerste afgestroop met Pd, Pt en dan Au wat daarop volg. Dit is presies die teenoorgestelde orde waarin die metale geabsorbeer word. Die voorafbehandeling met sianied, het ook n beduidende effek op die stroping van Cu. Dit kan verduidelik kan word aan die hand van die verskillende koper sianied komplekse wat vorm wat elkeen n verskillende affiniteit het vir adsorpsie. Wanneer 2% NaCN en 0.6% NaOH in die vooraf behandeling stap gebruik word, het die teenwoordigheid van koper geen negatiewe invloed op die afstroping van die PGMs gehad nie maar die herwinning is wel met 10% en 18% verlaag by 5 BVs wanneer geen sianied in die voorafbehandeling stap gebruik is nie.

Wanneer 100 mg/L KSCN sout by die adsorpsie stap gevoeg word, daal die herwinning van die PGMs in die stropings stap van 90% tot 70% by 4 BVs. Die addisionel K^+ katione verminder die herwinning met slegs 4% by 4 BVs wat beteken dat die vorming van adisionele komplekse soos $[Pt(SCN)_4]^{2-}$ en $[Pd(SCN)_4]^{2-}$, wat nie op die normale metode afgestroop kan word, n moontlikheid mag wees.

N maksimum van 0.15% vir Pt, 0.28% Pd en 0.6% Au word in die vooraf behandelings stap af gestroop. Indien die temperatuur van hierdie stap verhoog word na 80°C, verhoog die hoeveelheid Pt en Pd wat na hierdie stroom raporteer na n beduidende 8% tewyl Au basies onveranderd bly by 0.8%. Vir geaktiveerde koolstof wat hoër gelaai is (7000 mg/Kg Pt en Pd) en dus n beter

verteenwordiging van aanleg kondisies is, het 0.07% Pt, 0.11% Pd en 0.12% Au raporteer na die vooraf behandelings stap. Dit word toegeskryf aan die verspreiding van die PGMs op die koolstof wat hoofsaaklik op die oppervlakte voorkom en alhoewel die hoeveelheid klein is, word n sekere hoeveelheid slegs afgewas.

Dit is dus vasgestel hier, dat die afstroping van Pt n twee stap proses is. Die eerste stap is die voorabehandeling van die koolstof met n sianied oplossing en daarna volg die afstroping van die Pt met suiwer water teen ongeveer 80°C. Met die ontwikkeling van n wiskundige model, is bevind dat die snelheid waarteen die Pt afgestroop word, beinvloed word deur die hoeveelheid Pt en Na wat op die koolstof oppervlakte is, asook die konsentrasies van die metale in die vloeistof. Dit word wiskundig beskryf deur n gemodifiseerde Freundlich isotherm vergelyking asook deur die massa diffusie vergelyking. Die Pt afstropings snelheid wat afhanklik is van die Na konsentrasie kan vergelyk word met die afstroping snelheid van Au wat ook afhanklik is van die Na konsentrasie (Van Der Merwe and Van Deventer, 1990, Stange, 1990). Verder is bevind dat die snelheid van Pt stroping afhanklik is van beide die ewewig van Pt ione by die koolstof-vloeistof grens asook die massa beweging van Pt ione van die koolstof-vloeistof grens na die vloeistof. Beide hierdie snelheids bepalende faktore word bepaal deur die Na konsentrasie en skuif soos wat die Na konsentrasie verander soos wat die afstroping plaasvind. Vier hoof tyd periodes word gebruik om hierdie verskynsel te verduidelik. Deur die proses fundamenteel te verstaan, kan uiteindelik lei tot n beter proses, beter beheer, korter afstropings tye, kleiner toerusting of die ontwikkeling van n kontinue proses.

Acknowledgments

My sincere thanks go to:

My supervisors Prof Steven Bradshaw and Prof Guven Akdogan for their excellent guidance and continuous support.

Prof Jacques Eksteen for his mentoring, motivation and guidance on all aspects. Prof Eksteen, it is a privilege to have you as a mentor.

Western Platinum Ltd for their financial support.

Belinda Lombard, Ashley Hartzenberg and Paul Joubert for their excellence, hard work and assistance in completing the isotherm and repeat elution-, high temperature consecutive adsorption and high temperature elution experiments respectively. Your work has contributed a great deal to the completion of this thesis.

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

Alternative processing options, specifically related to the platinum and palladium industry, which follows the conventional mill-float-smelt-refine process routes to extract and refine PGMs (Pt, Pd, Rh, Ru, Ir and Au), that are less energy intensive and are more able to deal with complex, lower grade ores, are in demand. The Platreef orebody, to the north west of Mokopane in South Africa, is such an ore body, and with the exception of Anglo Platinum, which is currently the only company that is mining this orebody and blending this concentrate with concentrates from UG2 and Merensky resources for smelting, it remains undeveloped. The Platreef orebody is between 20 and 100 metres thick and dilution mostly derives from calcium silicate xenoliths. The traditional MF2 (mill-float-mill-float) approach to concentrating require high mass pulls for an acceptable recovery, which lead to low PGM concentrate grades, which are high in iron and sulphide. This, in turn, requires a very large investment in smelting, gas handling and acid (or alternative sulphur capture) plant infrastructure to produce a low grade matte (Eksteen et al. 2012).

According to Liddell and Adams (2012) there are potentially considerable technical and economic advantages to a robust hydrometallurgical processing route for PGM concentrates and the need for such a process. The need for an alternative process, which is specifically relating to Platreef ore types, is made clear when considering the twenty-two process flow sheets, that were evaluated by Adams et al. (2011) in a search for a more suitable process than the conventional mill-float-smelt-refine route. Mwase et al. (2014) proposed a promising heap leach process, which consists of a first stage base metal (BM) bioleach, followed by a precious group metal (PGM) cyanide leach step as a potential alternative route to process Platreef ore directly by circumventing the energy intensive steps of milling, floating and smelting. The primary bottle neck in this process currently is the relatively low extraction of Pt (58% on -6mm ore over 60 days) with the rate of Pt leaching from sperrylite in particular being a problem.

Preceding the PGM industry, Dreisinger (2006) found that, due to intensified research and development, hydrometallurgical treatment of copper concentrates is now making inroads to a field dominated by pyrometallurgical processes since the 1800s. Although difficult, this serves as a reminder and encouragement in the pursuit for a more cost effective PGM processing method.

1.1 A PGM cyanide leaching process

Leaching of PGMs (Pt, Pd, Rh, Ru, Ir and Au) with cyanide has been proposed a number of times as a promising PGM process option. The most recent references are those of Mwase *et al*. (2012a, 2012b and 2014), who explored a new process to extract PGMs from low grade concentrate or ore using a sequential stage heap leach process entailing heap bioleaching and high temperature cyanide leaching. The heap bioleaching extracts the base metals and Mwase et al. (2014) found

that 93% Cu, 75% Ni and 53% Co could be leached at 65°C after 304 days, whilst only 33% of the iron leached from crushed ore (-6mm+1mm). The residual iron was found to remain in the heap mostly as jarosite. After the bioleach the heap needs to be reclaimed, rinsed and the pH adjusted to a value of around 9.5 – 11 to ensure minimum loss of cyanide as hydrogen cyanide for the subsequent cyanide leach to extract Pt, Pd and Au. By maintaining a temperature of 55°C for the cyanide leach experimentation, it was found that 57.8% Pt, and 99.7% of the Pd and 90.3% of the Au could be leached within 60 days (Mwase *et al*. 2014). Heap leaching in the past has proven to be a very cost effective process for the treatment of lower grade ores and has been used extensively for the treatment of copper, nickel, gold etc. type ores (Kappes, 2002, Saari and Riekkola-Vanhanen, 2011). The heap leaching of ores containing gold and silver with cyanide solutions has been in use for a number of years, followed by a well developed precious metal recovery process (Au and Ag) from the cyanide solutions by carbon adsorption (CIP or CIL) or by the precipitation onto zinc (Merrill-Crowe) (Heinen et al. 1978).

Chen and Huang (2006) and Huang et al. (2006), also proposed a two-stage process, but instead of heap leaching, investigated selective pressure leaching cementation from low-grade Pt-Pd sulphide concentrates. It was found that for flotation concentrates, containing about 80 g/t Pt and Pd, after pre-treating by pressure acid leaching, followed by two steps of pressure cyanide leaching at 160°C, up to 90–94% Pt and 99% Pd, could be achieved.

Still on flotation concentrates, Platinum Australia Limited (PLA) in conjunction with Lonmin Plc (Lewins, 2003), developed the Panton Process, in which low grade flotation concentrates are subjected to low temperature calcination (275 - 550°C), followed by cyanide leaching at elevated temperature (60°C) to dissolve the PGMs, gold and base metals. These are then recovered from solution by precipitation (Bax, 2004) to produce a high grade PGM (4000 g/t) and base metal concentrate suitable as direct feed to a refinery. On Panton Project ores the process gave significantly higher recoveries (80% Pt and >95% Pd and Au), and resulted in much higher final product grades than standard flotation recoveries for the same material.

McInnes et al. (1993) and Bruckard et al. (1992) studied the ambient and elevated temperature cyanidation of ore from the Coronation Hill deposit in Australia, and found a maximum recovery of 80% Pt, 90% Pd and >95% Au at 125°C at a pH of 10 after a leach time of 6 hours.

Cyanidation of PGMs can also be applied to other related industries. According to Chen and Huang (2006) and Shams et al. (2003), the recovery of PGMs from automobile catalysts (an industry that is one of the main consumers of PGMs), is an area that has received much attention. Shams et al. (2003) reported that, among the vast variety of methods available, the cyanide leaching method for spent catalysts is more cost effective and environmentally friendly than conventional melting and acid recovery techniques.

By summarising the above mentioned literature on the cyanide leaching of Pt and Pd, it seems that recoveries, especially for Pt, are still problematic, but progress into the understanding of cyanide

leaching of PGM containing ore concentrate, as well as the growing recycling market, has been made. Though the leaching step has been investigated, research regarding the upgrading and recovery of the PGM cyanide leach liquor with activated carbon has received little attention.

1.2 Upgrading and recovery of PGMs from a cyanide leach stream

Although the leaching of PGMs has sparked interest in the past, very little is known about a suitable upgrading and recovery process such the adsorption of PGM cyanides onto activated carbon. When the effect of thiocyanate and base metals is included, together with dilution ranges found in heap leaching, no information could be found in the open literature.

It has been shown (Eksteen et al. 2014, Mwase *et al*. 2012a, 2012b and 2014) that a cyanide solution can also be used to leach PGMs (Pt, Pd, Rh, Ru, Ir and Au) and it is hypothesised here that the pregnant leach solution can be processed in a similar manner to the gold process through the adsorption of the formed metal cyanide complexes onto activated carbon or resin or by the precipitation onto zinc. Gold processing methods were evaluated and an initial flow sheet superstructure (Figure 1.1) was developed to serve as guideline to the possible options for the recovery of PGMs from a cyanide solution. Figure 1.1 does not represent one flow sheet but incorporates all the possible process options that were considered at the start of the project.

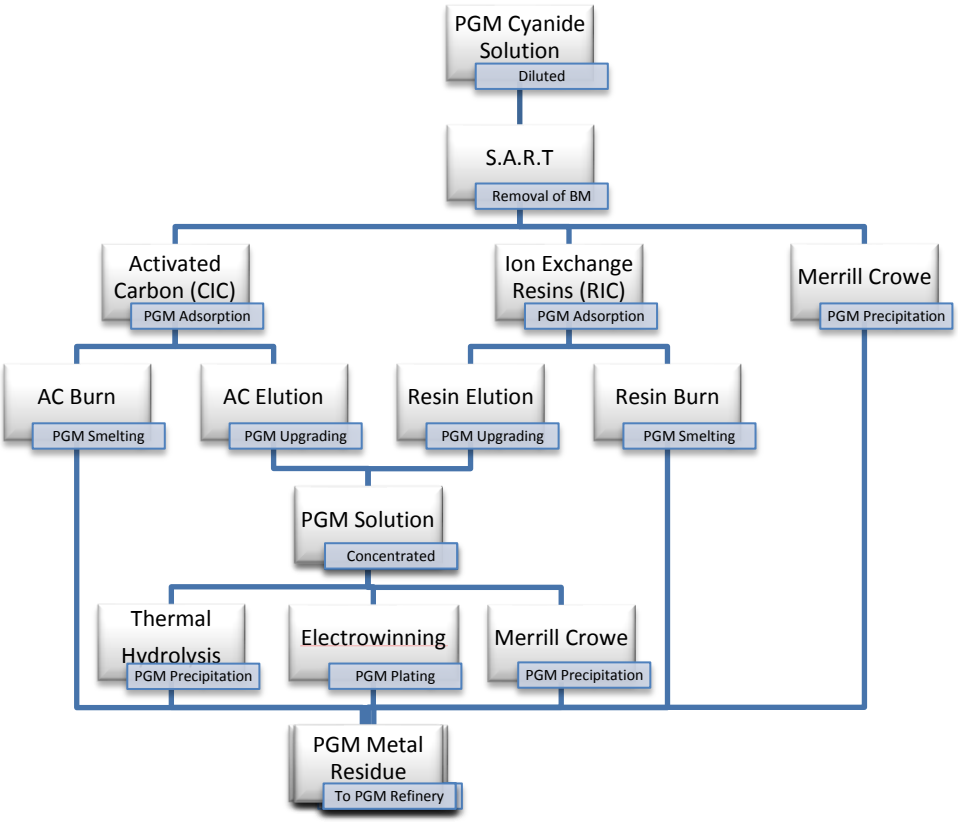


Figure 1.1: Flow sheet superstructure for the possible process routes for the recovery of PGMs from a cyanide solution.

The Merrill Crowe cementation process was investigated (Mpinga et al. 2014) and found to result in low recoveries for Pd (54%) and Pt (19%) while showing high recovery for Au (91%). Ion exchange was also investigated and found to be a viable option (Schoeman, 2012) for further consideration and the activated carbon adsorption process forms the main focus of the present study.

According to Tu et al. (2011), from the many techniques for the separation and concentration of Au, solid phase extraction using activated carbon is still preferred on account of the fast, simple and direct application, the high pre concentration factor, rapid phase separation and the cost saving that is associated with it. From the wide variety of sorbents available, activated carbon is still by far the most important, because of its large surface area, high adsorption capacity, porous structure, environmentally friendly, low cost and high purity standards.

Although the carbon adsorption process is well developed for the Au industry, several key questions arise for consideration of a similar process for the recovery of Pt and Pd.

- Will Pt and Pd be adsorbed from dilute concentrations (< 1 mg/L) onto activated carbon and what will the rate of adsorption be?
- How much Pt and Pd will adsorb onto activated carbon and will it be sufficient for a PGM upgrading process?
- What are the major factors that affect the adsorption of Pt and Pd?
- Can Pt and Pd cyanide complexes be efficiently eluted from activated carbon and how will it be done?
- Do conditions exist under which PGM CN complexes do not elute?
- What are the factors affecting the rate of elution?
- How will a Pt and Pd cyanide upgrading process look like and in which streams and in what grades will the Pt and Pd be?

1.3 Objectives

The adsorption and elution of gold cyanide using activated carbon have been studied extensively. It is believed that a process similar to the very popular gold CIP process can be used to extract platinum and palladium from low grade ores. Some research suggests that platinum and palladium will adsorb effectively onto activated carbon and rhodium to a lesser extent. The equilibrium adsorption isotherms and major factors affecting this process have not been determined, however, and no data regarding the elution of these species is available. Since it was the development of the elution process of gold from activated carbon that made the technology industrially feasible and led directly to the industrial implementation of the technology, this step is therefore of utmost importance if carrier phase extraction of PGMs using activated carbon is to be applied to the platinum industry.

The specific objectives of this study therefore are:

- To determine equilibrium adsorption isotherms for platinum and palladium cyanide complexes.
- To investigate the major factors affecting the adsorption of platinum and palladium.
- To determine the feasibility of eluting platinum and palladium from activated carbon.
- To determine the most important factors (such as temperature, pressure, cyanide concentration and ionic strength) affecting the elution of platinum and palladium.
- To develop a mathematical model for the elution of at least one of the metals in question namely either platinum or palladium from activated carbon to investigate rate limiting steps.
- To evaluate the model by testing it against the elution data obtained from laboratory experiments.

1.4 Scope and limitations

The scope of the project is limited to the investigation into the feasibility and development of a carbon adsorption and elution process for Pt and Pd cyanide complexes from a heap leach solution for which the content and solution concentrations were estimated from laboratory scaled experiments in a previous study (Mwase *et al*. 2012a, 2012b and 2014). Several factors which are deemed important will be included in the research across both the adsorption and elution stages and as such, detailed explanations and research into each of the mechanisms occurring will not be possible. The aim of the study is first to determine the feasibility of the carbon process and secondly to propose a set of important parameters that is likely to influence the process substantially. Optimisation of the carbon process, development of an optimised process flow sheet and comparison to other suitable technologies, falls outside the scope of the present study.

1.5 Thesis Overview

The first Chapter in this thesis presents the need for a new PGM processing method and the potential advantages of a hydrometallurgical route. The hypotheses (Eksteen et al. 2104, Mwase *et al*. 2012a, 2012b and 2014) of leaching PGM ore with a cyanide solution and upgrading through carbon adsorption and elution is discussed, and although the leaching aspect of this proposal has received some attention, the method and practicality of upgrading and recovery of the dilute PGM leach solution is predominately lacking. This forms the main objective of this research.

Chapter 2 gives an overview of the different carbon adsorption circuits used for gold extraction, after which a more detailed review of gold leaching chemistry is given. A short description of the understanding of PGM leaching with cyanide is also given. Background information on activated carbon is given and the two main steps of the activated carbon process for gold, namely adsorption and elution, are discussed in detail. For both of these steps, the associated mechanism and factors affecting the gold process are discussed and all the available research regarding the adsorption of

PGMs onto activated carbon is summarized, which will be used as a guide for the investigation into an adsorption and elution process for Pt and Pd. No information regarding the elution of Pt and Pd from activated carbon is available. The physical properties of the metal cyanide complexes, which will form the basis of this study (Pt, Pd and Au), as well as related metal cyanide species complexes (Cu, Ag, Ni, Hg, Rh etc.) are reviewed and, where available, the adsorption and elution behaviour of these complexes included as well. A summary of the literature review is given and the significance thereof discussed.

The experimental and analytical methods followed are outlined in Chapter 3. This Chapter identifies the materials used and the preparation of the materials that were required. It also describes how each of the experiments were performed, the experimental conditions that were involved and how the sampling was done. The repeatability of the experiments is also included in this Chapter.

Chapter 4 presents both the findings of the experiments, as well as the detailed discussion of each of the results. Pt and Pd equilibrium isotherms are given and the affect of important factors such as the temperature, cyanide concentration and base metals under continuous loading conditions, as would be the case in an industrial circuit, is given and discussed. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images of loaded activated carbon is studied to characterise the carbon surface. An elution method for Pt and Pd is proposed and the major factors affecting this process are discussed. The Pt and Pd deportment for each of the steps involved is given.

Chapter 5 continues from the previous Chapter, but focuses specifically on the elution of Pt from activated carbon by modelling this process mathematically in order to determine the equilibrium and film diffusion constants during the elution process.

Chapter 6 summarises the main conclusions from the adsorption and elution work performed and highlights the contributions made during this study. Recommendations for future work are made in Chapter 7.

References are listed and additional data supporting the findings in Chapter 4 and 5 is given in Appendix A. Experimental raw data for each individual experiment is given in Appendix B. Appendix C contains the data concerning the development of the Pt elution model ,while appendix D contains the calculations used for determining elution recovery. Appendix E provides a list of publications resulting from this research.

1.6 Contribution

This research covers a topic specifically of interest to the Pt and Pd industry and is considered to have great potential significance for future application. The thesis was the first comprehensive study on the application of activated carbon for the recovery of Pt and Pd from a cyanide leach solution, and covered a wide range of aspects for the establishment of such a process.

The thesis provides several answers for the adsorption process such as Pt and Pd adsorption capacity, rate of adsorption at various plant conditions and adsorption efficiency with diluted

streams under continuous adsorption conditions (as would be the case in an industrial circuit), and provides good insight into the factors that affect this process.

Where none existed, a procedure for the stripping (elution) of the adsorbed Pt and Pd cyanide complexes is established by using an analogue of the AARL technique. The factors affecting this process were investigated and the optimum conditions given where this process is expected to operate at. The data will enable the calculation of PGM upgrading ratios to determine concentrated stream grades, which can ultimately be used for the establishment and/or sizing of a suitable PGM-cyanide to PGM-metal step (such as electrowinning in the case of gold).

Chapter 2

Analogue processes and associated metals review

In order to effectively answer the questions as set out in the previous chapter and develop a suitable process for the adsorption and elution of PGMs using activated carbon, it is imperative to understand each unit operation of potential flow sheets, which primarily entail the leaching process, adsorption and elution and each of the factors affecting these steps, and how these steps influence each other. Analysis of the reactions, stabilities, structures and adsorption and elution capabilities of associated metals are included as a means of obtaining insight into the mechanism of adsorption and elution of platinum and palladium cyanide complexes onto carbon.

2.1 PGM mineralogy

Three South African ore types, as described by Cramer (2001), are mainly exploited for their PGM values: the Merensky reef, the UG2 reef, and the Platreef. The first two reefs are found in relation to one another with the generally wider UG2 reef lying below the Merensky reef by anywhere from 15 meters to 330 meters. In general, the PGM mineralogy is complex with a large number of sulfides, arsenides, tellurides, and alloys, which have been identified. The primary base metal minerals are chalcopyrite, pendlandite, and pyrrhotite and the PGM can be associated with the base metal sulfides, the various oxides, and the silicates.

For the Merensky reef, grades vary from 3–9 grams per tne (g/t) PGMs. Nickel can assay as high as 0.2% with some of the nickel found as a non-sulfide nickel and copper assays are approximately 0.1%. The more common PGM minerals in the Merensky reefs are braggite [(PtPdNi)S], cooperite (PtS), moncheite [(PtPdNi)$(TeBiSb)_2$], and kotulskite [(PtPdNi)$(TeBiSb)_2$].

For UG2, grades vary from 3–8 g/t PGM, with generally much poorer nickel and copper values than the Merensky reefs, but typically 25– 50% more rhodium and chromite than the Merensky reef. Valuable minerals also have significantly smaller average grain sizes and require fine milling for full liberation.

The Platreef in the northern area near Potgietersrus is wide, reaching widths of 50–90 meters in places and outcropping with a steep dip of 40–45 degrees. Grades are lower on average, at 2– 5 g/t, but with higher nickel and copper grades of 0.2–0.3% and 0.15–0.20% respectively. The PGM mineralogy is more complex and tellurides and arsenides are more common than in the Merensky or UG2 reefs. Sperrylite (PtAs2) is the most common PGM mineral. Platinum-palladium ratios are typically 1:1 within the Plat reef.

As discussed in Chapter 1, a new process proposed by Eksteen et al. (2014), Mwase *et al*. (2012a), (2012b) and (2014) revealed the potential effectiveness of a two-stage heap leaching process to extract PGMs and BMs (base metals) from a complex ore body (such as the Platreef ore body). The

first stage entails a bioleach process utilizing thermophilic microorganisms, operating at a temperature of 65°C, to extract BMs from the concentrate material after which the heap is reclaimed, neutralised and re-stacked for a cyanide heap leach as per Figure 2.2.

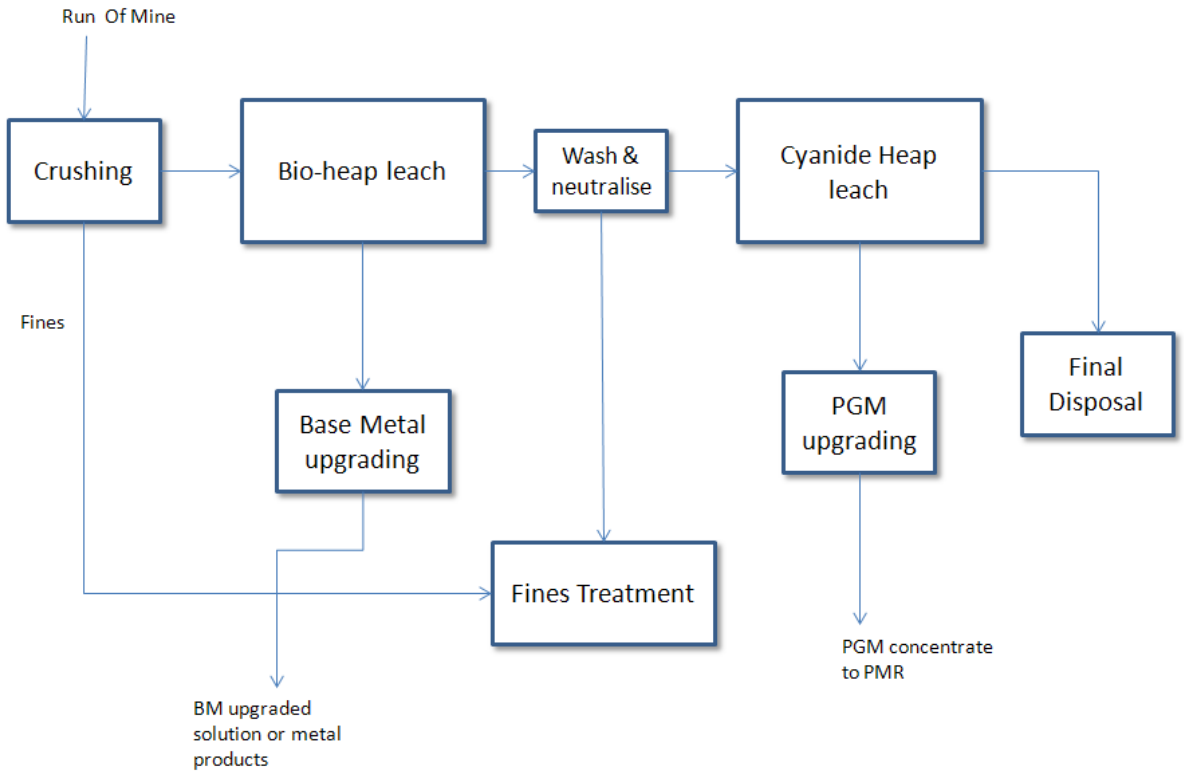


Figure 2.2: A simplified version of the proposed two staged heap leach flow sheet for the processing of Platreef ores

Currently there are no operating processes that recover platinum, palladium and gold from cyanide leach solutions as valuable high grade products that can be toll refined, or fed directly to a precious metal refinery. There are, however, well-established process options for the recovery of gold from dilute cyanide solutions such as the carbon-in-solution (CIS), carbon-in-pulp (CIP) and carbon-in-leach (CIL) process.

2.2 The carbon adsorption process for Au

According to Fleming (1992), the Merrill Crowe process was the primary method of gold and silver recovery for the first 70 years of the previous century. In more modern times, the carbon-in-pulp or carbon-in-leach (CIP and CIL) processes use activated carbon to adsorb the aurocyanide complexes directly from a milled slurry. This effectively eliminate the need for a solid/liquid separation step, which is one of the major disadvantages of the Merrill-Crowe process, and since the development of a carbon stripping method, this process has been the main commercial process on almost every gold plant built since 1980. (Fleming, 1992, Van Deventer, 1984). The carbon-in-solution follows basically the same route except that the carbon adsorbs aurocyanide from a solution instead of the slurry and are therefore applicable to the heap leach process. Major advantages of carbon adsorption plants are that they require lower capital and operating costs, are

mechanically robust, handle plant upsets remarkably well and are highly tolerant to changes in feed composition (Fleming et al. 2011).

For these reasons, the carbon adsorption process has become well established since the 1980s, and considerable progress has been made in understanding the mechanisms and kinetics of adsorption onto activated carbon (Van Deventer, 1995). The subsequent steps of elution and electrowinning have also received much research attention (Van Deventer et al. 1995, Van Deventer et al. 1993, Soleimani and Tahereh Kaghazchi, 2008, Banini and Stange, 1993, Brandon et al. 1986, Costello 2005) with the relatively old references indicating that the technology for gold is quite mature. In order to understand how PGMs will be adsorbed and eluted from activated carbon, there will be potential advantage in understanding the well established mechanism of gold adsorption and elution.

A block-flow diagram of a typical carbon adsorption plant for a non refractory gold ore is shown in Figure 2.3 indicating the difference between CIP (milling, thickening, leaching) and CIS (heap leach).

For both of the options, the ore from the mine is first reduced in size by crushing to ensure the gold is liberated and accessible for cyanide leaching. For CIP/CIL, the ore is milled where-after the slurry is thickened to increase the pulp density to approximately 50 % solids by mass, which in turn reduces the size of the leaching plant. The pH of the pulp is adjusted to a value of around 9.5 – 11 to prevent the formation of hydrogen cyanide, which is both toxic as well as result in the loss of expensive cyanide. The leaching of gold with sodium cyanide and oxygen takes place in a series of agitated leach reactors (Stange, 1999). The leaching of the gold is represented by the Elsener equation:

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH \qquad (2.1)$$

After leaching, the pulp is passed over screens to remove all unwanted material like woodchips and plastics before adsorption takes place.

The alternative to this flow section is heap leaching of the gold ores. Cyanide heap leaching is typically for exploiting low-grade ores or deposits too small to justify the construction of above mentioned, milling, thickening and leaching facilities. Cyanide leach solutions are sprayed onto the heaps, which consist of either run-of-mine material or crushed material, with the pregnant solution collected at the bottom of the heaps on water tight pads. The basic principle of the cyanidation process and described by equation 1 is still followed for heap leaching. (Heinen et al. 1978)

After leaching the pulp flows through a cascade of well mixed adsorption tanks, typically 6 to 8 in number. Conventional practice is to have a mean pulp residence time of about an hour in each tank. The tanks are normally mechanically agitated and each will contain a batch of carbon of concentration ranging from 10–25 grams of carbon per litre of pulp (0.5 to 1.2% by volume carbon). The carbon is retained in each reactor by means of screens having an aperture of 0.6–0.8 mm, that allows pulp to flow through and out of the reactor, whilst retaining the carbon in the reactor. The gold aurocyanide complex in the aqueous phase is readily adsorbed onto the activated

carbon. The pulp (or leached solution) and activated carbon are moved in a counter current flow arrangement. As the carbon moves up the train, it is contacted with higher concentrations of the gold in the pulp or solution, while the gold in the less concentrated solution is adsorbed by the fresh activated carbon. By the time the pulp leaves the last tank in the adsorption cascade the concentration of gold in the aqueous phase is typically between 0.001 and 0.02 mg/L with a value of 0.01–0.005 mg/L regarded as a practically achievable value for most well designed and operated plants. This represents a gold recovery of 90–99% depending on the tenor of the feed solution. (Stange, 1999)

The carbon in the reactor into which pregnant pulp is fed (referred to as the first reactor) becomes highly loaded with gold. Loaded carbon values on operating plants range from 300 to 20 000 grams of gold per t of carbon with a concentrating factor of about 1 000–1 500. A portion of the loaded carbon is periodically removed from the first adsorption reactor for elution. This produces a small volume of solution with a high gold concentration. The gold is recovered from this solution mostly by electrowinning (Stange, 1999).

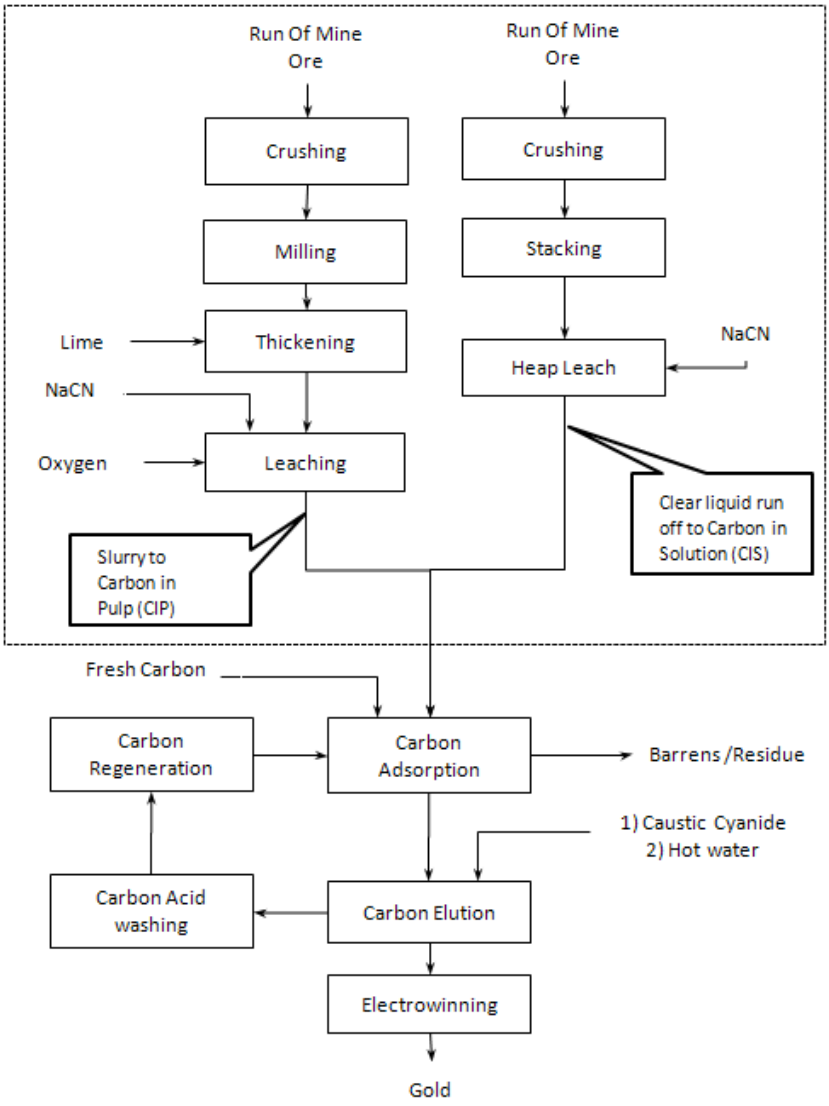


Figure 2.3: The Carbon adsorption process for the extraction of Au

2.3 Cyanidation

2.3.1 Cyanidation of gold

Cyanide is the most widely used lixiviant applied to dissolve gold from its ores, and because the gold exists mainly in the elemental form, similar cyanidation conditions are generally applicable to most gold ores according to McInnes et al. (1994). Oxygen, through adding hydrogen peroxide solution or bubbling pure oxygen or air through the pulp, oxidises the metallic gold to form soluble Au^+ cations, which are in turn strongly complexed by cyanide ligands (CN^- anions) forming the aurocyanide complex ion $[Au(CN)_2]^-$, which is described by the Elsener equation as already discussed above (Mwase, 2009).

According to Finkelstein (1972), as referenced by Van Deventer (1984), most of the gold dissolves by the reaction:

$$2Au + 4NaCN + O_2 + 2H_2O \rightarrow 2NaAu(CN)_2 + H_2O_2 + 2NaOH \quad (2.2)$$

and only a small portion dissolves via the Elsener equation [2.1]. Whether the cyanidation of gold occurs through either of the above mentioned reactions, the same aurocyanide complex is formed in both cases, which are important for the following adsorption and elution sections.

Cyanide, however, is not selective to gold and will also complex with silver as well as copper, nickel and the other BMs, which usually occur in greater amounts in the ore than gold and are predominantly present as sulphides. The estimated mineral distribution of typical Witwatersrand ores in South Africa ranges from 5 – 9% sulphides, 3 – 8% chlorides and 81 – 88% quartz. The sulphide minerals in the ore are various distributions of pyrite, pyrrhotite, chalcopyrite and other base metal sulphides (Lorenzen and Van Deventer, 1992).

According to Marsden and House (2006), most metal sulphides decompose quite readily in aerated, alkaline cyanide solution to form metal cyanide complexes and various sulphur-containing species like thiocyanate. The general reaction for a sulphide containing a divalent metal cation is given as follows:

$$2MS + 2(x + 1)CN^- + O_2 + 2H_2O \rightarrow 2M(CN)_x^{(x-2)-} + 2SCN^- + 4OH^- \quad (2.3)$$

Thiocyanate (SCN^- , that forms during Eq. 2.3) has also been considered as an alternative lixiviant to cyanide, and will therefore also react to form a complex with gold in the presence of Fe^{3+} or peroxide as oxidant according to the simplified reaction (Aylmore, 2005):

$$Au + 4SCN^- + 3Fe^{3+} \rightarrow Au(SCN)_4^- + 3Fe^{2+} \quad (2.4)$$

Reaction 2.4, however, occurs mainly at potentials of around 0.4–0.45V and at a pH of between 1 and 3. $Au(SCN)_4^-$ is more likely to form at the upper limit of the potential range with $Au(SCN)_2^-$

forming with a decreasing potential. Gallagher et al. (1990) showed that $Au(SCN)_2^-$ will adsorb onto activated carbon, but is then reduced to metallic gold on the carbon surface. Subsequently, water does not elute dithiocyanatoaurate(I) at all and chemical re-dissolution of the metallic gold is required. The $Au(CN)_2^-$ complex is also more stable than the $Au(SCN)_2^-$ complex (Aylmore, 2005) and the $Au(SCN)_2^-$ complex is therefore unlikely to form when sufficient free cyanide is available and when the pH is high (>9) as in typical CIP conditions. The $Au(SCN)_4^-$ complex, however, is more stable than the $Au(CN)_2^-$ complex (Aylmore, 2005) and in the unlikely event that this complex does form, it may be difficult to elute. According to Davidson et al. (1979), when present in the solution, thiocyanate anions have a very detrimental effect on the rates and capacity constants of gold adsorption.

Kononova et al. (2007) found thiocyanate to complex with silver and, depending on the thiocyanate concentration, can form a precipitate of AgSCN or $Ag(SCN)_2^-$ and $Ag(SCN)_3^{2-}$. The silver thiocyanate complexes were found to adsorb onto carbon, but could also not be eluted efficiently with water.

2.3.2 PGM cyanidation

According to Mwase (2009), it has been experimentally shown that PGM cyanidation occurs in the same manner as that of gold. Platinum(II) and palladium(II) form stable complexes with cyanide, namely $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ (McInnes et al 1994, Hancock et al. 1977). Although higher pressures and temperatures are in some cases required for PGM cyanidation, the reactions reported also follow the Elsener equation (Chen and Huang 2006):

$$2Pt_{(s)} + 8NaCN_{(aq)} + O_2 + 2H_20 \rightarrow 2Na_2[Pt(CN)_4]_{(aq)} + 4NaOH_{(aq)} \quad (2.5)$$

$$2Pd_{(s)} + 8NaCN_{(aq)} + O_2 + 2H_20 \rightarrow 2Na_2[Pd(CN)_4]_{(aq)} + 4NaOH_{(aq)} \quad (2.6)$$

$$4Rh_{(s)} + 24NaCN_{(aq)} + 3O_2 + 6H_20 \rightarrow 4Na_3[Rh(CN)_6]_{(aq)} + 12NaOH_{(aq)} \quad (2.7)$$

Eq. 2.5 to 2.7 will be more related to leaching recycled PGM catalysts but in the case of the PGMs being present as a sulphide, the reaction will follow Eq. 2.3 to form the same cyanide complexes of $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$. Although the impurities and stream grades may be different, the similar complexes that form indicate that a carbon adsorption and elution process may be applicable to cyanide leach solutions where the source of Pt and Pd are from either a recycled product or from ore.

With the primary base metal minerals associated with PGM ore being chalcopyrite, pendlandite, and pyrrhotite as described in section 2.1, these metals, if not removed, are also expected to leach concurrently with the PGMs and form metal cyanide complexes and thiocyanate (as per the previous section), which will be present in the subsequent adsorption section.

2.4 Activated Carbon

Carbonized wood, which by present day standards can be regarded as a crude form of activated carbon, has been in use for many years. Ancient Egyptians (1500 B.C) and Hindus used it for medicinal and purifying purposes, and since then it has found many applications in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications.

McDougall (1991) and Van Deventer (1984) describe activated carbon as a generic term for a family of highly porous carbonaceous materials, that cannot be characterized by a structural formula or by a chemical analysis, but are known for their ability to adsorb, due to their extremely porous nature resulting in a very large internal surface area. Activated carbon can be manufactured from almost any source of carbonaceous material such as peat, lignite, coconut shells, coal, fruit pits, wood, bones and many more. The different types of activated carbon can be distinguished from one another by properties such as the number and size distribution of the pores, bulk density, hardness, abrasion resistance and particle size distribution. Coconut shell and extruded coal based charcoals are most commonly used in the gold industry, mainly due to their extremely good impact hardness and wet abrasion resistance combined with their high adsorptive capacity for the small gold dicyanoaurate complex. (McDougal, 1991, Van Deventer, 1984, Van der Merwe, 1991)

The pore structure consists of irregularly shaped spaces between the microcrystallites as well as larger openings and has an extended surface area of between 600 and 1500 m^2/g. (Van Deventer, 1984)

Activation is the process by which the carbonized product develops the extended surface area and porous structure, and is generally conducted thermally at temperatures between 800 and 1000°C. (McDougal, 1991). After adsorption in a gold CIP circuit the activity is reduced mainly, due to organic constituents originating from mine waters. These organic poisons in the used carbon are firmly bound to the carbon and are not removed by elution, but only by thermal means. (Davidson and Duncanson 1977) This step is referred to as re-generation or re-activation and is an important part for all CIP process plants recycling the activated carbon.

2.4.1 Effect of carbon type

One important difference between activated carbons, which is a function of the source material (peat, lignite, coconut shells, coal, fruit pits, wood, bones), is the total pore volume. The pores can be classified in terms of their diameters into macropores (500 – 20000 nm), mesopores (100 – 500 nm) and micropores (8 – 100 nm) (Van der Merwe, 1991), but are usually just referred to as macro or micropores.

Fisher and La Brooy (1997) investigated acid washing of an extruded peat based activated carbon and a coconut shell based activated carbon, that was loaded with gold and nickel, to a similar extent. The pore volume of the coconut based activated carbon was found to be almost double to

that of the peat based activated carbon, which resulted in three times faster Ni extraction with acid.

Poinern et al. (2011) investigated the use of waste macadamia nut shells for the production of an activated carbon for commercial use. A similar affinity for the auro cyanide complex to commercially used coconut based activated carbon was found, and it was suggested that, because of the higher strength of the macadamia shell, compared to coconut shell, it could be with some optimisation of the activation process, become an alternative to coconut based activated carbons. Further optimisation was required to improve the hardness of the macadamia nut product. These factors point to the fact that the source material for activated carbon is important and may even point to differences between activated carbons from coconut shells originally grown in different soils with different weather conditions.

In addition to the expected physical differences and differences in kinetics and equilibrium adsorption capacities between activated carbons of different source materials, Van Deventer and Van der Merwe (1993) found that an important difference between the adsorption mechanisms, proposed by different authors (specifically whether $[Au(CN)_2]^-$ will decompose to AuCN), is the type of activated carbon used. Adsorption results were found to depend not only on the type of source material for the activated carbon, but also on the supplier, as well as on the specific batch from a specific supplier. In other words, different batches from the same manufacturer may result in different results, especially with regards to the species formed on the activated carbon.

Specifying the properties, supplier, as well as the specific batch, is therefore important in any adsorption and elution experiments and a variable that needs to be constant during experimentation.

2.4.2 Regeneration of activated carbon

Thermal regeneration of activated carbon is the process of restoring the carbon activity by burning off the organic foulants, that accumulate during adsorption and elution, and is necessary for the continual removal of gold in CIP and CIL circuits (Adams, 1991, Urbanic et al. 1985). Adams (1991) describes the carbon activity as the term that encompasses both the kinetic and thermodynamic aspects of the affinity for adsorption onto a given carbon.

Van Deventer and Ross (1991) have found that the duration and temperature of regeneration should be determined by the nature of the organics adsorbed on the activated carbon. Hence, it is possible that regeneration conditions could differ dramatically between plants.

2.5 Adsorption onto activated carbon

The adsorption step is critically important as the Au, that is not adsorbed during the adsorption stages, is seen as a loss as it reports to the tailings. Several authors (Van Deventer, 1994, Van der Merwe, 1991) have also found that a very important factor for the elution process is actually the

adsorption process and knowledge of the form in which the species adsorb, the distribution thereof through the carbon particles and the depth to which the species have penetrated into the porous structure of the carbon determines the method with which it will elute.

2.5.1 The mechanism of adsorption

According to Steinfeld et al. (1998), adsorption occurs on a solid surface, and is due to the attractive forces between the surface and the adsorbed specie (adsorbate). The two broad types of adsorption are chemical adsorption and physical adsorption. In chemical adsorption, the adsorbed species form a chemical bond with the adsorbent, while in physical adsorption the forces involved are relatively weak intermolecular forces or Van der Waals forces (Steinfeld et al. 1998, Ruthven, 1984). The general features, which distinguish these two adsorption processes are as per Table 2.1.

Table 2.1: General features to distinguish between physical and chemical adsorption (after Ruthven, 1984)

Physical Adsorption	Chemical Adsorption
Low heat of adsorption	High heat of adsorption
(< 2 or 3 times latent heat of evaporation)	(> 2 or 3 times latent heat of evaporation)
Non specific	Highly specific
Mono or multi layer	Monolayer
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low temperatures	Possible over a wide range of temperatures
Rapid, non-activated, reversible	Activated, may be slow and irreversible
No electron transfer although polarization of adsorbate may occur	Electron transfer leading to bond formation between adsorbate and surface

According to both Ruthven (1984) and Steinfeld et al. (1998), the distinction between these two mechanisms is not always clear and that there are many intermediate cases.

The mechanism of adsorption onto activated carbon seems to be such a case and is not a very straight forward matter as many researchers have found. Van Deventer (1984) stated that although much work has already been completed regarding the adsorption of various organic and inorganic species, the theories regarding the mechanism still remained the matter for much controversy. Mpinga, (2012) recently found this still to be the case and that no complete agreement of the adsorption mechanism exists. The main reason for this is that chemical changes in the adsorbate or surface oxide groups are difficult to monitor, because activated carbon cannot be investigated by direct physical procedures such as infrared spectroscopy or X-ray diffraction (McDougall et al.1980, Van Deventer, 1984) The most widely accepted theories are: (Adams, 1991)

1. adsorption involving ion pairs, $M^{n+}[\ Au(CN)_2^-]_n$
2. adsorption of unpaired $[Au(CN)_2]^-$ ions onto activated carbons

3. decomposition to other species such as AuCN, Au or a partially reduced state.

According to Adams (1991), the above mentioned mechanisms have all been shown and can operate under various conditions of ionic strength, pH value, and oxygen concentration. Between the adsorption mechanisms of $M^{n+}[Au(CN)_2^-]_n$ and adsorption at cationic sites on the carbon surface by ion exchange, the ion pair adsorption of $M^{n+}[Au(CN)_2^-]_n$ is definitely the favoured one, especially at typical CIP conditions (Adams, 1991). This conclusion is supported by the fact that a neutral molecule such as $Hg(CN)_2$ competes very effectively with $Au(CN)_2^-$ for adsorption sites.

Evidence against the chemical degradation of aurocyanide to AuCN and of other species on the carbon surface is listed by Adams (1991), with the main argument against the degradation of aurocyanide, being the analysis of loaded activated carbon by Mossbauer spectroscopic investigations indicating that the gold presents on the activated carbon as the $Au(CN)_2^-$ ion. It is also stated that no commercial activated carbon products are sufficiently powerful reducing agents (E = -0.16 to 0.16 V) to reduce the aurocyanide ion (E^0= -0.79 V). Adams (1991), however, also states that loading under acidic conditions does lead to some decomposition of $[Au(CN)_2]^-$ to Au(CN). Evidence of the decomposition of silver cyanide on activated carbon at typical elution temperatures to a silver metal or precipitate has also been found by Costello (2004), suggesting that even if the reduction or decomposition of the metal cyanide species on the activated carbon is not the main mechanism of adsorption, it is still very likely that different forms metal cyanide forms are present on the carbon.

Van der Merwe (1991) specifically placed emphasis on this and stated that an important difference between the proposed mechanisms for adsorption is the character of the adsorbed species. For gold, possible absorbed species include, $NaAu(CN)_2$, $HAu(CN)_2$, $Au(CN)_2^-$, AuCN and Au with $Au(CN)_2^-$ and AuCN (with or without cations) as the most likely species at typical CIP operating conditions. Allthough both these species adsorb onto activated carbon, the elution of these species is different, with $Au(CN)_2^-$ being the specie that will elute with water. The nature of the adsorbed species in this study is deemed important, as one of the functions of the AARL pre-treatment step rests upon the principle that cyanide is used prior to elution with water to ensure that the gold species adsorbed onto the activated carbon is converted to the soluble $[Au(CN)_2]^-$. Cyanide free elution is therefore possible if all the gold adsorbed onto the carbon is already in the elutable form. Knowledge of the form in which species adsorb, or the form it is in on the activated carbon under specific conditions, will therefore determine the nature and extent of the pre-treatment step.

The nature of the adsorbed species on the activated carbon and specifically whether degradation from $Au(CN)_2^-$ to AuCN occurs, remain discussion points especially, as mentioned above, most authors have substantiated their conclusions adequately by thorough experimentation. Van Deventer and Van der Merwe (1993) ascribed these different results from different authors to the different samples of activated carbon used. Through elution tests, FTIR scans(Fourier Transform Infrared Scan) and XPS analysis (X-ray Photoelectron scans), they found that different batches of carbon have different tendencies of converting $Au(CN)_2^-$ to AuCN.

Although some disagreement among authors regarding the mechanism of adsorption still exists, knowledge of the form in which species are adsorbed, the kinetics of the adsorption and the stability of these complexes are still deemed essential to determine suitable and optimized elution methods.

2.5.2 Distribution on activated carbon

Pleysier et al. (2008) studied microtomography images of an activated carbon grain loaded with 2500 mg/kg gold, a typical loading observed in a gold plant and found that at these gold loadings, adsorption predominantly takes place at the external surface of the carbon particles. The initial adsorption rate is therefore fast and determined by the diffusion of gold cyanide through the hydrodynamic boundary layer surrounding the carbon particle (film diffusion) to the external surface.

When saturation of the external surface is approached, surface diffusion of the gold particles into the centre of the carbon particle becomes the rate limiting step and adsorption slows down significantly. Saturation of the external surface, however, only seems to occur at very high gold loadings at around 25000 mg/kg as indicated by Pleysier et al. (2008) and Vegter (1992). Vegter (1992) also found that at these high gold loadings, after about 2 days of adsorption, a uniform distribution of gold throughout the carbon particle was found. According to Vegter this is an indication that uniform distribution of gold (or at least some loading on the centre of the particle) will be obtained in carbon particles in a typical extraction plant with an average residence time for carbon of several days or 1 week. It is also interesting to note that Pleysier et al. (2008) observed that the gold penetration into the activated carbon is uniform for the macro and micro pores which can be described by surface diffusion.

Van der Merwe (1991) investigated the effect of the distribution of adsorbed gold on the desorption thereof, first at room temperature and then at conditions more favourable for the desorption of gold (70°C with cyanide pre-treatment). It was found that the rate of elution was higher for carbons, that were loaded with gold over a shorter period of time (steeper gold concentration gradients or in other words gold that loaded predominantly near the surface), than carbon where more time for the diffusion into the carbon was allowed. At stronger elution conditions, the elution rate was found to be less sensitive to negligible to the distribution of the gold on the carbon particle.

2.5.3 Factors affecting the adsorption onto activated carbon

The factors affecting the adsorption of gold cyanide have been studied extensively and only a brief discussion on some of them is given below.

2.5.3.1 Temperature

The adsorption of gold onto activated carbon is an exothermic process and an increase in temperature will therefore shift the equilibrium to favour elution or desorption. (Van Deventer et al. 1994) Temperature is also considered by a number of authors (Van Deventer, 1993, Adams and Nicol, 1980, Davidson, 1974) to be the most important factor in the efficient elution of gold and other metal cyanides from activated carbon.

Van der Merwe (1991) found that the equilibrium loading on activated carbon decreased significantly with an increase in temperature from 22°C to 60°C and found an Arrhenius relationship between the temperature and the equilibrium gold loading (Freundlich istotherm constant A) on carbon BTX (AC from Beatrix mine, South Africa).

$$A = 0.019 \exp \frac{2190}{T} \qquad (2.8)$$

Fleming and Nicol (1984), also found that the rate of loading will increase as the temperature of the solution increases but that the loading capacity will decrease. At 20°C, the adsorption rate constant of 3400 h^{-1} with an equilibrium capacity of 73 000 mg/kg was reported which was increased to 4900 h^{-1} as the temperature increased to 62°C but the equilibrium capacity decreased to 35 000 mg/kg. The pH for these experiments were reported to be 10.5 with 0 free cyanide and 30 mg/L of Au. Activation energy of approximately 10 kJ/mol was calculated.

2.5.3.2 Influence of Cyanide concentration

Woollacott and Guzman (1993), confirmed findings by Nicol et al. (1984) and Davidson et al. (1982) that an increase in cyanide concentration will decrease the equilibrium gold loading. This effect was found to be more pronounced when the cyanide concentration is low (below 10 mg/L) and the decreasing effect was less pronounced at cyanide levels from 10 to 50 mg/L NaCN. Woollacott and Guzzman (1993), however, found that the latter was only true when the oxygen concentration was above 5.5mg/L. Adams, 1991, state that not only does the loading capacity decrease with an increase in the cyanide concentration but that the rate of loading also decreases.

2.5.3.3 pH

Fleming and Nicol (1984) and McDougal et al. (1980) observed that the equilibrium loading of gold cyanide is enhanced by lowering the pH. Petersen and Van Deventer (1991) concluded that a lower pH tends to make the carbon surface more acceptable for metal cyanides as well as organics. Higher pHs will therefore favour the desorption process with the pH of elution circuits typically being in the range between 12 and 13. According to Van Deventer et al. (2003), the pH will remain fairly constant at a specific temperature during the elution process. Similar to the cyanide concentration, Fleming and Nicol (1984) found that the rate of loading also increased as the pH of the solution decreased. The effect on the capacity is, however, much greater that the effect on the rate. Rate constants of 3010 h^{-1} with an equilibrium capacity of 75 000 mg/kg was reported for an pH of 11.3 which was increased to 4880 h^{-1} with an equilibrium capacity of 216 000 mg/kg at an

pH of 1.5. The ionic strength for these experiments were reported to be 0.2 M with carbon sizes of between 0.5 to 0.7 mm, stirred at 1250 rpm with 30 mg/L of Au.

2.5.3.4 Oxygen

The presence of oxygen has generally been found to have a positive effect on the adsorption of metal cyanide complexes. Woollacott and Nino de Guzman (1993) summarized the understanding of the influence of oxygen as follows:

1. An increase in oxygen will lead to an increase in the equilibrium loading, but without a change in adsorption kinetics (Petersen and Van Deventer, 1991).
2. The effect of dissolved oxygen is greater in solutions with low ionic strength than when the ionic strength is high, although some disagreement was found to the extent of this effect (Adams, 1990, Woollacott and Nino de Guzman, 1993).
3. When the cyanide concentration is high (>100mg/L), the effect of changes in the oxygen concentration on the equilibrium is more pronounced when the oxygen concentration is low.

Adams (1991) stated that the enhanced adsorption at low ionic strength is attributed to the formation of positevly charged ion-exchange sites on the carbon surface. In plant situations, which usually operate at high ionic strength, the presence of oxygen enhance gold loading more indirectly by the catalytic oxidation of cyanide, thereby removing species that depresses adsorption.

2.5.3.5 Ionic strength

Fleming and Nicol (1984) found that as the ioninc strength of the solution increase, the rate of loading as well as the loading capacity also increases. Similar to the pH, the effect on the capacity is, however, much greater that the effect on the rate. Rate constants of 3150 h^{-1} with an equilibrium capacity of 56 000 mg/kg was reported for an ionic strength of 0.005 M which was increased to 4150 h^{-1} with an equilibrium capacity of 113 000 mg/kg at an ionic strength of 1 M. The pH for these experiments was reported to be 6.5 with carbon sizes of between 0.5 to 0.7 mm, stirred at 1250 rpm with 30 mg/L of Au.

2.5.4 PGM adsorption onto activated carbon

Aguilar et al. (1997) studied the adsorption kinetics of precious metal- cyano complexes onto activated carbon through their newly developed capillary electrophoresis (CE) method and found that Pt (II) and Pd (II) cyanides were selectively adsorbed onto carbon in a short time (100%), while Rh (III) cyanides showed much lower adsorption (40%). Roijals et al. (1996) also found that Pt adsorbs fairly quickly onto activated carbon and, in addition, studied the PGM adsorption potential of several impregnated and ion-exchange resins. Desmond et al. (1991) evaluated the loading of activated carbon with PGMs and found that more than 99% of the Pt and Pd, but less

than 15% of Rh, were removed from solution. From these initial Pt and Pd adsorption studies, the possibility of an adsorption process seems promising, but a significant amount of data, such as kinetic rate data, adsorption capacity, upgrading potential, initial concentration impact and the influence of impurities, is lacking.

Recent studies by Mpinga (2012) confirmed the findings by the above mentioned authors. Pt and Pd adsorption efficiency and recovery were studied as a function of different adsorption parameters, such as solution pH, copper concentration, nickel concentration, free cyanide ion concentration, thiocyanate concentration, initial PGM (Pt, Pd and Au) ion concentration and activated carbon concentration.

Adsorption rates for platinum, palladium and gold from a solution with low concentrations of PGMs (Pt – 0.15 mg/L, Pd – 0.38 mg/L, Au, 0.1mg/L, Rh – 0.01mg/L) onto 10 g/L of carbon were very high within the first 60 minutes (giving more than 90% extraction of precious metals) and thereafter continued to adsorb at a slower rate until a pseudo-equilibrium was reached or close to 100% adsorption was obtained after 72 hours. Among the different adsorption parameters, nickel concentration was found to have the most significant effect on the adsorption process, followed by the adsorbent concentration. Adsorption of Ni was found to proceed at approximately the same rate and with the same recovery as the precious metals, showing a recovery of approximately 90% in two hours. The Cu adsorption kinetics was slower, with less than 30% being recovered after 120 minutes. Due to the relatively low amount of free cyanide present (12 mg/L), it is expected that a mixture of the slower adsorbing $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$was present.

Mpinga (2012) observed no significant changes in the solution concentrations of Rh and Fe (less than 5% adsorption) after 72 hours. Mpinga (2012) stated that at such low solution concentrations, it is possible that Rh reaches equilibrium very rapidly at a concentration where analytical errors are significant. Snyders et al. (2013) expected that Rh was present in the solution as an octahedral $Rh(CN)_6^{3-}$ (Aquilar et al. 1997), which is a strong cyanide complex with a stability constant of 47 (Read et al. 1994). This was compared to the similar strong cyanide complexes of $[Pt(CN)_4]^{2-}$ with a stability constant of 40 and $[Pd(CN)_4]^{2-}$ at 51.7 (Monlien et al. 2002), which do adsorb well, and it was therefore considered likely that the low adsorbance of Rh is due, either to the high negative charge of $Rh(CN)_6^{3-}$ or the shape and size of this molecule. In the case of Fe, the very low adsorption is supported by Vorob'ev-Desyatovskii et al. (2012), who showed that neither $K_3[Fe(CN)_6]$ nor $K_4[Fe(CN)_6]$ in neutral and alkaline (pH 10.5) aqueous solutions are adsorbed on an activated carbon (GoldcarbWSC207C-GR). In the study of the effect of free cyanide on the adsorption of PGMs, experimental results by Mpinga (2012) indicated that there is no change in the adsorption behaviour of the PGMs system between 100 and 300 mg/L CN^- for the first two hours of adsorption. The cyanide concentration is expected to have a more significant effect on PGM adsorption under continuous loading conditions and further investigations are deemed important.

Davidson et al. (1979) stated that thiocyanate anions were shown to have a detrimental effect on the rates and capacity constants of gold adsorption, when added individually to a synthetic solution at concentration levels of approximately 100 g/t as found in the plant solution. However, Mpinga

(2012) found that the presence of 100 mg/L SCN^- did not appreciably affect the adsorption of PGMs. This observation is supported by the selective and quantitative extraction of Pt, Pd and Au from the column leach liquors containing 3670 mg/L SCN^- as discussed by Mpinga (2012). Further investigations in this direction were deemed warranted.

Mpinga (2012) found the affinity of activated carbon for metal ions to follow the selectivity sequence as expressed below.

$$Au(CN)_2^- > Pt(CN)_4^{2-} > Pd(CN)_4^{2-} > Ni(CN)_4^{2-} > Cu(CN)_3^{2-}$$

Vorob'ev-Desyatovskii et al. (2012) suggested that a strong contribution to this difference in adsorption between metal cyanide complexes is attributed to the geometry of the complex. Linear complexes like $[Au(CN)_2]^-$, $[Ag(CN)_2]^-$, $[Cu(CN)_2]^-$ and $Hg(CN)_2$ adsorbs strongly onto activated carbon, while planar complexes like $[Pt(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ to a lesser extent (Mpinga, 2012) followed by distorted planar complexes such as $[Cu(CN)_3]^{2-}$. Tetrahedral ($[Cu(CN)_4]^{3-}$, $[Ag(CN)_4]^{3-}$, $[Zn(CN)_4]^{2-}$, $[Cd(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$) and octahedral complexes ($[Rh(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Pt(CN)_6]^{2-}$) do not adsorb onto activated carbon. According to Vorob'ev-Desyatovskii et al. (2012), adsorption occurs through the formation of metallophilic metal-metal bonds and forms 'columns' of complexes with linear molecules with alternating ions turned at a right angle to each other, while planar complexes form 'stacks'. The formation of the metallophilic metal-metal bonds between cyanometallate complex anions with tetrahedral or octahedral structure, however, is deemed impossible and the reason why these complexes don't adsorb.

As opposed to the above mentioned examples, Adams (1992) found that the affinity of carbon for $[Au(CN)_4]^-$, which has a planar structure (Shorrock et al. 2003), is greater than for the linear $[Au(CN)_2]^-$

2.6 Elution

According to Banini and Stange (1993) elution is one of the principal unit processes in the carbon-in-pulp (CIP) process and the carbon adsorption method only became practical on development of a usable method for stripping the gold from activated carbon so it could be recycled in the system (Heinen et al. 1978, Van der Merwe, 1991).

There are mainly three types of elution methods used in practice (Van Deventer et al. 1993, Adams, 1991, Banini and Stange, 1993, Van der Merwe, 1991):

1. The Zadra Process is primarily the circulation of warm (90°C - 95°C) cyanide solution (0.5% NaCN and 1 to 2% NaOH typically) through the elution column and electrowinning cells for several hours (50) at atmospheric pressure until an acceptable barren solution is reached. High pressure Zadra at 120°C to 140°C is also practised but requires cooling to below 100°C before electrowinning.

2. The AARL Process consists of a hot acid wash followed by a hot (100 - 120°C) caustic cyanide pre-treatment step (0 to 5% NaCN and 2% NaOH typically) for 30 min and afterwards elution with hot de-ionized water at high pressures (200 – 300 kPa). The rate of elution is significantly faster taking only 6 – 8 hours for satisfactory elution. The solution passes through the column only once and is collected in a storage tank from where it is circulated to the electrowinning cells.
3. Elution with organic solvents, that involve combinations of the above mentioned processes.

Since the two main Au elution methods both use a caustic cyanide solution at high temperature, they could be seen as variations from each other. The AARL method, however, allow for decoupling of the elution and electrowinning sections and since no method for the electrowinning of Pt and Pd has been developed yet, the AARL method was chosen as basis for the current study. The outcome of the study on the AARL technique here would then dictate the necessity for further research and development work.

A typical AARL gold elution profile at 70°C as determined and discussed by Van Deventer et al. (1994) can be seen in Figure 2.4. The concentrations of the gold, cyanide and potassium have been normalised for comparative reasons. Van Deventer et al. (1994) highlight the sharp decline in the cyanide and potassium concentrations within the first two bed volumes and ascribe the tailing effect due to the reagents being trapped in the pores of the carbon. A bed volume (BV) is defined here as the empty volume of the reactor, that is occupied by the packed bed of carbon. The peak in the gold profile only appears once the bulk of the pre-treatment reagents has been removed. The pH remains high for the whole duration of the run, even though the pH of the water supply has not been adjusted.

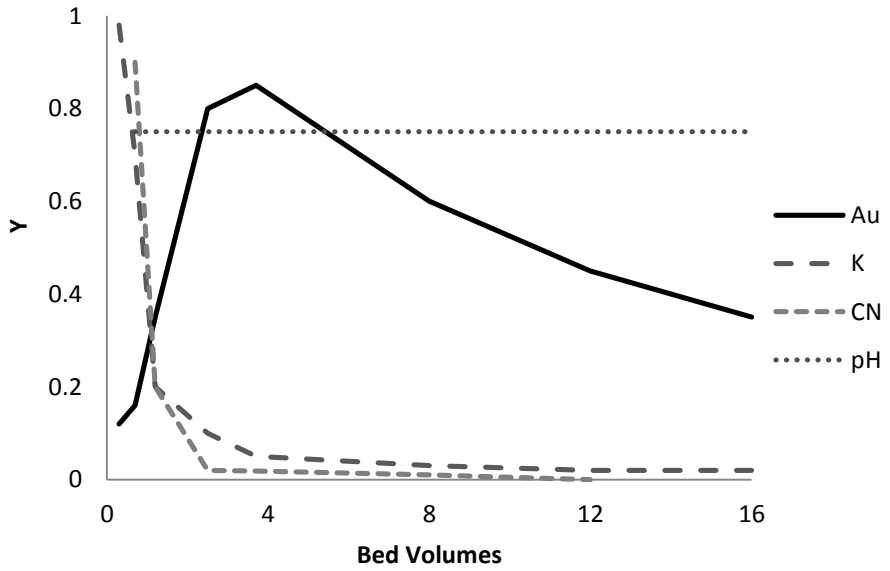


Figure 2.4: A typical AARL elution profile at 70°C for carbon containing 4.83 g/kg Au, [Au] = 140.Y mg/L, [K^+] = 3500.Y mg/L, [CN^-] = 1500.Y mg/L, pH = 14.Y (redrawn from Van Deventer et al. 1994).

2.6.1 The mechanism of elution

The mechanism of adsorption has been discussed earlier. Under typical plant conditions, it is most likely that aurocyanide is adsorbed as a chemically unchanged ion pair of the form $M^{n+}[Au(CN)_2^-]_n$.

Adams (1991) and Van Deventer and Van der Merwe (1994) agree that the adsorption process is a thermodynamically reversible process and that the chemical and the physical factors, that inhibit the adsorption, will enhance the elution and vice versa.

Adams and Fleming (1989) and Adams (1991) suggested that the mechanism of elution involved the ionization (or partial ionization) of the phenolic-type groups on the surface of the activated carbon by sodium hydroxide. This causes the surface of the activated carbon to become negatively charged and therefore unable to adsorb the aurcocyanide ion pair. In addition, it was argued that not only phenolic groups, but also carboxylic groups are present on the activated carbon surface. In a similar mechanism, the cyanide ion reacts with the carbonyl groups and results in the formation of additional negatively charged sites on the activated carbon surface.

Van Deventer and Van der Merwe (1994) argued that the presence of high concentrations of spectator cations (M^{n+}), as in the AARL pre-treatment step, depresses the desorption of aurocyanide by the formation of the neutral $M^{n+}\{Au(CN)_2^-\}_n$ species on the carbon. The elution of the aurocyanide is therefore largely dependent on the removal of these cations (M^{n+}) from the carbon after the pre-treatment step. Furthermore Van Deventer and Van der Merwe (1994), came to a conclusion similar to that of Adams and Fleming (1989) regarding the function of cyanide, and stated that the cyanide during the pre treatment step reacts with the functional group on the carbon surface and essentially passivates the carbon surface for the adsorption of metal cyanide complexes, and that it is the passivation and not the free cyanide carried over, which causes the elution of the metal cyanide complexes. The degree of passivation is determined by the cyanide concentration (up to an optimum point), the temperature of the pre-treatment step and most probably the time of the pre-treatment step (which will also reach a plateau) and also affects the elution of the cations.

An additional function of the cyanide in the pre-treatment step is, that if reduction to an irreversible specie (such as AuCN) or even stronger adsorbing species ($[Cu(CN)_2]^-$ compared to $[Cu(CN)_3]^{2-}$) occur, cyanide will also react with these species to obtain an elutable complex. The occurrence and ratio of these species have been found dependent on the type of activated carbon and/or the conditions of the acid washing step.

2.6.2 Factors affecting the elution of activated carbon

The factors influencing the rate of elution have also been the topic of much research and are summarized by Adams (1991) as:

1. Temperature
2. Cyanide and Hydroxide concentrations
3. Ionic strength
4. The design of the elution column

5. Effect of impurities
6. Concentrations of gold eluate
7. Elution time and flow rate
8. Recycling of eluate
9. Organic solvents
10. Effect of acid washing prior to elution
11. Cyanide decomposition
12. Irreversibly adsorbed species (Van Deventer et al. 1993)

The most important of these factors, according to Adams and Nicol (1986), in order of decreasing importance, are temperature, cyanide and hydroxide concentrations, and the ionic strength of the eluant. The irreversibly adsorbed species described by Van Deventer et al. (1993) are the stable AuCN and Au species and when present, will affect the elution rate and efficiency.

Although it is not really possible to quantify each parameter in islolation (Davidson, 1977, Van Deventer and Van der Merwe, 1993) a summary of the effect of each parameter will be given in the following sections.

2.6.2.1 Temperature

As stated previously, the elution temperature has been found to be an extremely important factor in the efficient elution of gold from activated carbon. By increasing the temperature of the eluate, the maximum concentration of the elution profile is increased and the dynamics of desorption are significantly enhanced according to several authors (Van Deventer and Van der Merwe, 1993, Davidson and Duncanson, 1997). This was found to be the case for all types of activated carbon. McDougal et al. (1980) related the reason for the more efficient elution of gold at higher temperatures to the more than 14 times higher solubility of $KAu(CN)_2$ in hot (79°C) rather than cold water (22°C).

Van Deventer and Van der Merwe (1993b, 1994b) found, that not only the temperature of the eluate contributes to more efficient elution, but also the temperature of the cyanide pre-treatment stage in the AARL process. By comparing the elution of gold after pre treatment at 100°C to the elution profile obtained after pre-treatment at 20°C, it was found that the elution efficiency was improved with the higher pre-treatment temperatures, and it was postulated that more cyanide will decompose on the surface of the activated carbon at higher temperatures, which change the functional groups on the surface in such a way that the surface becomes less receptive for adsorption. With higher pre-treatment temperatures, the hydrolysis of cyanide is faster with the tempo of hydrolysis increasing, according to an Arrhenius relationship. These decomposition products of the cyanide can now render the carbon less susceptible to the adsorption of gold cyanide, which will result in the gold equilibrium becoming less sensitive to temperature after pre-treatment in cyanide at elevated temperatures. It could also be argued that the carbon simply retained its heat after a high temperature pre-treatment, but if this was the case, the effect would have been most obvious in the early stages of elution with an increased elution rate for the carbon

initially at the higher temperature. This is, however, not observed from the elution curve, but rather an equal rate of elution, initially with elution curve for the lower temperature pre-treatment flattening out sooner, and at a lower peak concentration, than for the carbon that was pre-treated at a higher temperature.

The cation concentration, which is also an important factor for elution, also seems to be of greater importance at higher temperatures, as the elution efficiency becomes more sensitive to the cation concentration as the temperature is increased, according to Van Deventer and Van der Merwe (1993b).

2.6.2.2 Cyanide and Hydroxide concentrations

Cyanide and hydroxide salts are added during both the AARL and Zadra elution procedures to enhance the elution of the gold cyanide. For both of these two elution procedures, the addition of cyanide will increase the elution kinetics until a maximum is reached. The decrease in the elution rate at higher cyanide concentration that follows, is ascribed to the opposing effects of cyanide and increasing ionic strength (Adams and Nicol, 1986, Van Deventer and Van der Merwe, 1994). Van Deventer and Van der Merwe (1994) showed that under conditions of constant ionic strength, which was maintained by the addition of NaCl, an increase in the cyanide and hydroxide concentrations just resulted in an increase in elution kinetics.

Competitive adsorption through the displacement of $[Au(CN)_2]^-$ by the CN^- has been ruled out by Van Deventer and Van der Merwe (1994a), as no significant elution takes place during the cyanide pre-treatment step. Furthermore, Van Deventer and Van der Merwe (1994a) found that the cyanide in the pre-treatment step is of greater importance than the cyanide that is present (which is mainly carried over from the pre-treatment step) during the actual elution. The peak in gold elution in the elution profile actually only occurs once most of the cyanide has been washed out of the system.

Allthough the general tendency is that cyanide will increase elution kinetics, different metal cyanide complexes, however, tend to react differently to the cyanide concentration. Boshoff (1994) showed that in some cases, for example when only a small amount of copper co-adsorbed (1200 g/t) or the ratio of copper to gold is small (<0.4), gold can be eluted without cyanide, but not in the case of high copper loadings (12000 g/t). Van Deventer and Van der Merwe (1993a) found that cyanide free elution was possible when all the gold remained as the $Au(CN)_2^-$ complex, but required cyanide when a conversion to AuCN on the activated carbon occured. The reason for the conversion of the aurocyanide complex may be either due to the activated carbon used and temperature or due to a hot acid pre-treatment step prior to elution. Copper and silver will form di-, tri – or tetra cyanide complexes at various levels of cyanide concentrations, which adsorb and elute differently. The effect of cyanide on each of the different metals is discussed in more detail in section 2.6.

Both Adams (1991) and Van Deventer and van der Merwe (1994a) agree that the effect of NaOH is considerably less than the effect of cyanide on the elution of gold from activated carbon, with Van

Deventer and van der Merwe (1994a) quantifying it at about 10 times less. (distilled water as eluant at 70°C, flow rate = 49.5 mL/h. Carbon = 9.41 g, carbon loading = 4.9 g Au/kg, pretreated in 20 mL of solution containing 12,300 mg K^+/l (as either KCN or KOH and KCl), pH of 12.3 at 20°C for 30 min). In practice, hydroxide is still added to the pre-treatment, but mainly to stabilize the cyanide to prevent the formation of toxic cyanide gas (HCN_g) (Van Deventer and van der Merwe, 1994a, Davidson and Duncanson, 1977).

2.6.2.3 Column Pressure

Jeffrey et al. (2009) showed that the column pressure does not have any effect on the elution process as long as the pressure is maintained above the vapour pressure of the eluant.

2.6.2.4 Ionic strength

The presence of dissolved salts in the pulp generally results in an increase in the loading capacity of carbon and the magnitude has been found to depend upon the type and concentration of the cation (Adams, 1991). McDougal (1980) and Van Deventer and Van der Merwe (1994a) reported the beneficial effect of the cations on the adsorption to be in the order $Ca^{2+} > Mg^{2+} > H^+ > Na^+ > K^+$. Conditions of a low ionic strength will therefore favour desorption and this is the basis for the use of de-ionized water in the AARL process. During the pre-treatment stage, it is also reckoned by Adams (1991) and Davidson and Duncanson (1977) that the hot caustic cyanide solution converts the stronger adsorbed calcium or Mg ion pairs into less strongly adsorbed $Na^+Au(CN)_2^-$ ion pairs.

From experiments performed by Van Deventer and Van der Merwe (1994a,b) the bulk of the desorption occurs only once the cation concentration is lowered. The horizontal position of the gold peak seen in typical elution profiles is therefore considered to be function of the kinetics of the removal of the cations carried over from the previous stages.

Davidson and Bailey (1991) demonstrated a significant effect of water quality on the elution of gold. It was found that as the water quality decreases, demonstrated specifically by an increase in Na^+ ions, the gold elution efficiency decreases dramatically.

2.6.2.5 Column design

Several factors can be incorporated into the column design section of which the length versus diameter ration of the column, the flow rate of the eluant, number of stages in the column and batch or continuous operation form part of.

Menne (1987) (as described by Van Deventer and Van der Merwe, 1994a) concluded from elution profiles, obtained from laboratory scale columns with a wide variety of height/diameter ratios, that no apparent effect could be found. The variations that did occur, especially on larger columns, were attributed to deviations from ideal plug flow. Van Deventer and Van der Merwe (1994) also found a

relative insensitivity towards the column geometry and rather used the elution profiles, obtained for different columns, to describe the amount of deviation from plug flow in the larger column.

Adams (1991), Van der Merwe (1991) and Van Deventer et al. (2003) found the elution efficiency of gold, silver and nickel, not to be seriously affected by the elution rates within which they experimented with. Some authors, however, found the elution efficiency to be affected by the elution flow rate under certain conditions with lower flow rates typically resulting in a higher stripping efficiency (Davidson 1975, Van Deventer and Van der Merwe, 1994a), while under other conditions found the flow rate to have little to no effect on the elution of gold.(Davidson and Duncanson, 1977, Davidson, 1986, Van Deventer et al. 2003) To explain this phenomena, Van Deventer and Van der Merwe (1994a) concluded that the sensitivity towards flow rate will decrease as the conditions become less favourable for adsorption, such as under strong pre-treatment conditions.

2.6.2.6 Effect of impurities

During cyanide leaching of gold ores, a number of base metals are also leached, notably copper, nickel, cobalt, iron and zinc. It has been found that the cyanide complexes of cobalt, iron (Mpinga, 2012) and zinc are not loaded well onto activated carbon, and their presence in solution has little effect on the extraction efficiency of gold. (Boshoff 1993)

The presence of adsorbed metals impurities such as copper, nickel and mercury can significantly reduce the carbon loading capacity for the precious metals, thereby necessitating a higher carbon inventory and more frequent elution with higher NaCN concentrations. Efficient gold elution is largely dependent on the efficiency with which copper is eluted, which in turn is related to the copper loading of the carbon.

The extent to which the elution process is therefore influenced by additional metal cyanide complexes depends greatly on the type of metal and metal cyanide complex , metal concentration, pH, cyanide concentration and temperature. The effect of each of the metal cyanide complexes on the elution process is therefore discussed individually in the subsequent sections.

2.6.2.7 Gold concentrations/Carbon loading

Davidson and Duncanson (1977) found that the higher the gold loading on the activated carbon, the more efficient is the elution process and ascribed it to the elution of gold with deionized water being a physical rather than a chemical displacement of equilibrium. Boshoff (1994), however, found the elution efficiency rather independent of the amount of gold present on the activated carbon. Van Deventer and Liebenberg (2003) found that the elution of gold became more difficult with an increase in loading. Van Deventer and Liebenberg (2003) described this observation as quite interesting and suggested two possible reasons:

1. As the amount of gold increases, clusters of gold form with stronger adsorption characteristics. No evidence for this hypothesis is provided by Van Deventer and Liebenberg (2003), but the idea of clusters of gold forming corresponds to Yin et al. (2011), who studied the hydration energies of aurocyanide and argentocyanide anions through molecular dynamic simulations (MDS) and stated that these anions tend to form clusters in water and may increase the adsorption onto activated carbon.
2. With an increase in the gold loading, the elution process shifts from equilibrium to being mass transfer controlled, the latter being slower.

2.6.3 Acid washing

The primary purpose of the acid washing step is to remove calcium build–up and other contaminants (Grimsley, 1991). Dilute hydrochloric acid, followed by rinse water, will remove impurities like calcium and zinc when cold and additional nickel, iron and silica when hot (90°C), but will not elute gold, copper and silver from the activated carbon according to Van der Merwe (1991) and Davidson and Baily, (1991). According to Davidson and Baily (1991) approximately 1 bed volume of 3 vol % hydrochloric acid will effectively remove calcium from the loaded carbon. Little or no elution of calcium takes place without an acid wash step. In cases where the loaded carbon contains high amounts of calcium carbonate, the acid washing of the carbon, along with the temperature, has been considered to be the most important factor for efficient elution (Davidson and Veronese, 1979).

The acid washing step is also the step where there is the least agreement among operators. The type of acid, acid strength, time, temperature, acid treatment vessel and placement of this step are all variables, that are different from the one site to the next, each with advantages and disadvantages. The placement of the acid washing step will also, to a large extent, determine the extent of the influence that each of the factors, discussed in the previous section, has on the elution process. The acid washing step is therefore discussed here independently of these 'factors', (Section 2.5.2) although it can also be considered as being one of them.

Several advantages of acid washing of the loaded carbon prior to the elution are listed by Davidson and Baily (1991):

1. The elution system's temperature can be increased through a hot acid wash without eluting any gold or silver from the activated carbon, which will increase the efficiency of the subsequent elution.
2. Severe calcium passivation can have a negative impact on the subsequent elution of gold, which will be eliminated through the acid washing step.
3. In the case of very high loadings of nickel, iron, and silica, as well as with effluent circuits operating at reduced pH levels, the acid washing step will reduce the reagent requirements. As these were not specified, the reagents referred to here are assumed to be the NaCN and NaOH in the pre-treatment step.

4. A significant advantage is the quality of water used for gold elution. Gold elution efficiency decreases with decreasing water quality, but a hot acid wash of the carbon prior to elution seems to de-sensitize the elution efficiency to water quality. A plausible explanation for the effect is related to the character of the gold species on the activated carbon according to the mechanism:

$$Ca[Au(CN)_2]_2 \overset{hot\ acid}{\rightarrow} AuCN \overset{pre-treatment}{\rightarrow} NaAu(CN)_2$$

5. Van Deventer et al. (1994) primarily agree with this mechanism and accept that the aurocyanide complex will be linked to the spectator cation introduced with the pre-treatment agents. The $Ca[Au(CN)_2]_2$ ion pair is more strongly adsorbed on the carbon than the $NaAu(CN)_2$ specie according to the cation absorbtion strength order, $Ca^{2+} > Mg^{2+} > H^+ > Na^+ > K^+$, described in section 2.5.4 and will therefore be more sensitive to conditions, that effect the elution thereof than the more readily elutable species.

Van Deventer et al. (1994), however, found much decreased elution results where an acid wash treatment commenced prior to the pre-treatment step. Although the carbon was rinsed with distilled water prior to the cyanide pre-treatment step, enough acid is said to have remained on the carbon to destroy a significant part of the cyanide, that is utilised for the gold elution. It was also found that the pH during elution dropped from 10 for the non-acid washed carbon to 9 for the acid washed carbon, which favours adsorption rather than elution. It is important to notice, however, that the carbon for the study by Van Deventer et al. (1994) was loaded from gold solutions containing no calcium and no hydroxide was added to the pre-treatment solutions.

Boshoff (1994) found that cyanide is required in the pre-treatment step if an acid washing step takes place prior to elution and consequently, the higher the copper loading on the activated carbon, the greater the need is for cyanide in the pre-treatment step for efficient gold elution. Regarding the acid temperature, lower gold recoveries were obtained when a 90°C acid wash step was performed, compared to a 25°C acid washing step with equal amounts of cyanide in the pre-treatment step. It was suggested that during the acid washing of copper loaded carbon, insoluble copper cyanide species form, which block the pores and reduce the gold elution efficiency. (Boshoff, 1994, Fisher and Labrooy, 1997) Cyanide in the pre-treatment step will convert these species to an elutable form again. These findings also correspond to the theory that partial conversion of $[Au(CN)_2]^-$ to AuCN occurs under acidic conditions with a higher degree of conversion at higher temperatures. In the case where cyanide (2%) was added to the pre-treatment step, Boshoff (1994) found that the kinetics of elution after a 90°C acid wash was faster than after a 25°C acid wash (although the overall recovery for the 90°C acid wash was lower). When no cyanide was present in the pre-treatment step, the elution kinetics for the 25°C acid wash was faster than for the 90°C acid wash. No explanation for this, however, was given. Boshoff (1994) did find that less calcium was removed after the 15 min cold acid wash, which may have a detrimental effect on the adsorption and elution performance due to the fixation of the calcium on the carbon during regeneration.

Fisher and Labrooy (1997) investigated the effect of nickel on the elution of gold from activated carbon and found that the acid washing of carbon loaded with nickel prior to elution can result in pore blockage by the formation of a $Ni(CN)_2$ precipitate, which has a detrimental effect on the gold recovery.

Similar molar concentrations of HCl (3%) and HNO_3 (3%) were compared, and it was found that washing the loaded activated carbon with HCl resulted in faster nickel desorption kinetics than with HNO_3 (Fisher and Labrooy, 1997). The reason for this is unclear, but it was hypothesised that, because HNO_3 is such a strong oxidant, it may either oxidise the carbon surface or react with the nickel cyanide complex, which slows down the removal of these species.

Comparative evaluation of industrial circuits is difficult due the difference in size, material treated (dump material or waste rock to run of mine ore), type of activated carbon used and the column size and geometry. Acid treatment procedures vary just as much and can range anything from 0.5 to 15 hours of a 1 to 5% acid concentration before or after or before and after elution from 25 to 90°C.

2.6.4 Most recent elution research

As can be seen from the references listed, most of the fundamental research regarding the elution process occurred in the 1980s and 90s. More recent research, specifically regarding elution of gold from activated carbon, mostly focused on improving the kinetics or economics of the current processes. Examples are the study of ultrasonic elution of gold from activated carbon (Feng et al. 2003), the use of different organic solvents as eluant (Soleimani et al. 2008) or the use of activated carbon produced from different raw materials than the conventional coconut shell activated carbon (Soleimani et al. 2005). Staunton (2005) states that most of the advances in the 10 years prior to 2005 have mainly been in the area of carbon management and that preference to cyanide free elutions was becoming apparent.

2.7 Metal cyanide complexes

In general, metal cyanide complexes are described as negatively charged ionic complexes consisting of one or more cyanide ions (CN−) bound to a single transition metal cation with a general formula $[M(CN)_b]^{x-}$. The chemical formulas and stabilities of some of metal cyanide complexes are shown in Table 2.2. Stability constants are a measure of the strength of the interaction between the reagents, that come together to form the complex, or otherwise stated, it is a measure of the extent to which the species will form or be transformed into other species. The higher the value of the stability constant, the more stable the complex and the less chance of the specie converting to another specie.

Vorob'ev-Desyatovskii et al. (2012) related the shape of the molecule to the selectivity of activated towards these molecules. Linear complexes adsorb strongly onto activated carbon, planar

complexes to a lesser extent, while almost no adsorption of tetrahedral and octahedral complexes takes place.

Table 2.2: Stability and shape of metal cyanide complexes

Complex	log K	Shape	Reference
$[Os(CN)_6]^{4-}$			De Haas et al. (1977)
$[Ru(CN)_6]^{4-}$			De Haas et al. (1977)
$[Co(CN)_6]^{3-}$	64		Dionex corporation. (2003)
$[Pd(CN)_4]^{2-}$	51.7	planar	Monlien et al. (2002), Vorob'ev-Desyatovskii et al. (2012)
$[Rh(CN)_6]^{3-}$	47	octahedral	Read et al. (1994), Aquilar et al. (1997)
$[Fe(CN)_6]^{3-}$	43.6	octahedral	Zang et al. (1997), Vorob'ev-Desyatovskii et al. (2012)
$[Pt(CN)_4]^{2-}$	40	planar	Monlien et al. (2002), Vorob'ev-Desyatovskii et al. (2012)
$[Au(CN)_2]^{-}$	36, 38 - 39	linear	Hancock et al. (1072), Phuddephatt (1978)
$[Au(CN)_4]^{-}$	56	planar	Millard (2005), Shorrock et al. (2003)
$[Fe(CN)_6]^{4-}$	35.4	octahedral	Zang et al. (1997), Vorob'ev-Desyatovskii et al. (2012)
$[Ni(CN)_4]^{2-}$	30	planar	Monlien et al. (2002), Millard (2005)
$[Cu(CN)_2]^{-}$	16.3 - 24	linear	Lu et al. (2002), Hancock et al. (1972), Millard (2005)
$[Cu(CN)_3]^{2-}$	26.4, 35	distorted planar	Hancock et al. (1972), Zang et al. (1997),
$[Cu(CN)_4]^{3-}$	23.1	tetrahedral	Millard (2005), Shorrock et al. (2003)
$[Ag(CN)_4]^{3-}$	21.9	tetrahedral	Zang et al. (1997)
$[Ag(CN)_3]^{2-}$	21.4,21.8	tetrahedral	Zang et al. (1997), Hancock et al. (1972)
$[Ag(CN)_2]^{-}$	20.5, 20.9	linear	Zang et al. (1997), Hancock et al. (1972)
$[Zn(CN)_4]^{2-}$	19.6	tetrahedral	Millard (2005), Vorob'ev-Desyatovskii et al. (2012)
$[Cd(CN)_4]^{2-}$	17.9	tetrahedral	Millard (2005), Vorob'ev-Desyatovskii et al. (2012)
$Hg(CN)_2$		linear	Vorob'ev-Desyatovskii et al. (2012)
$[Hg(CN)_4]^{2-}$		tetrahedral	Vorob'ev-Desyatovskii et al. (2012)

2.7.1 Copper

Numerous authors have studied the dissolution of Cu in the presence of cyanide. Ores containing a significant amount of copper minerals lead to copper solubilisation as cuprous cyanide complexes. This, according to Lu et al. (2002) can result in a significant economic penalty in excess cyanide consumption, loss of a valuable copper by-product and significant cost in cyanide destruction during effluent treatment.

The negative impact of copper ores on recovery of precious metals with the cyanidation process has, been known from almost the start of this technology (Shantz and Reich, 1977). The impact of the copper on the gold cyanidation process depends on the cyanide soluble copper, which is largely dependent on the amount and type of copper minerals present in the ore. The solubility of the

copper in the various types of ore ranges from 5.6% for chalcopyrite ($CuFeS_2$) to 95% for covellite (CuS) and Azurite ($2Cu(CO)_3.Cu(OH)_2$) (Shantz and Reich, 1977 and Ford et al. 2008). Regardless of the amount of cyanide soluble copper, the reactions of Cu^+ with cyanide have been described by Ford et al. (2008) as:

$$Cu^+ + CN^- = CuCN \quad (2.9)$$

$$Cu^+ + 2CN^- = [Cu(CN)_2]^- \quad (2.10)$$

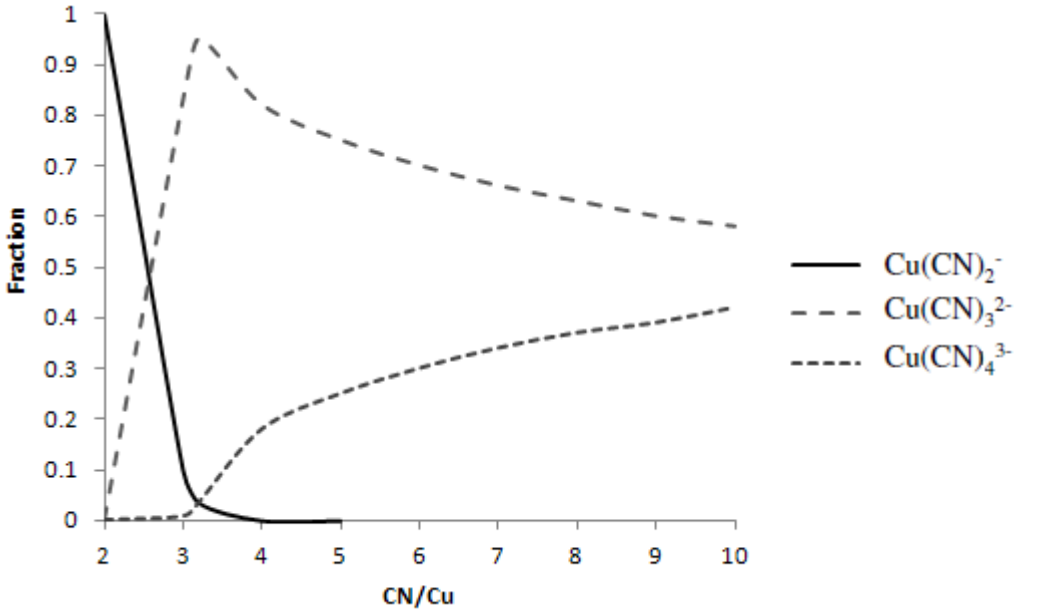
$$[Cu(CN)_2]^- + CN^- = [Cu(CN)_3]^{2-} \quad (2.11)$$

$$[Cu(CN)_3]^{2-} + CN^- = [Cu(CN)_4]^{3-} \quad (2.12)$$

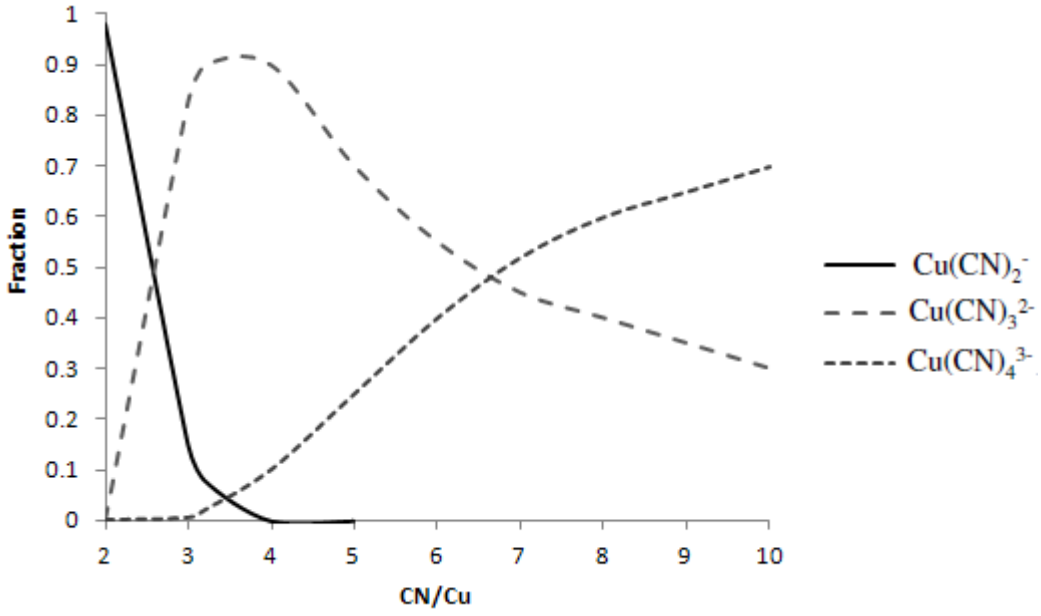
According to Boshoff (1994), Adams (1991), Lu et al. (2002) and Shantz and Reitz (1977) the occurrence of the above mentioned di-, tri- and tetracyanides of copper depends on the conditions such as pH, temperature, the mole ratio of copper to cyanide and the total copper concentration. Although the prediction of the predominant copper cyanide complex can be rather complex, a general guideline is that $[Cu(CN)_2]^-$ is favoured at low pH and low cyanide concentrations, whereas $[Cu(CN)_4]^{3-}$ is formed at pH above 10 and cyanide strengths above 200mg/L. $[Cu(CN)_3]^{2-}$ is the most stable form of copper cyanide and is usually the dominant complex found in typical plant solutions. The solid precipitate of CuCN as per reaction (2.9) is produced at a pH below 3 (Ford et al. 2008). Souza et al. (2014) found that at a pH of 10.5 and a CN/Cu molar ratio of 2.5, the $[Cu(CN)_2]^-$ species are stable and present. It was also observed that from a CN/Cu molar ratio of 4 at pH 10.5, the formation of the $[Cu(CN)_4]^{3-}$ species gradually increases as the CN/Cu molar ratio increases, while the amount of $[Cu(CN)_3]^{2-}$ species gradually decreases. At a CN/Cu molar ratio of 10, only the $[Cu(CN)_4]^{3-}$ species were observed (Figure 2.5). The thermodynamic stability of these complexes can be seen in the Eh-pH diagram in Figure A.141 in Appendix A.

Copper is not only a consumer of expensive cyanide in the leaching stage, but also causes problems in the downstream adsorption, elution and electrowinning circuits. Considering the above mentioned complexes, it has been found that the $[Cu(CN)_2]^-$ will load strongly onto the carbon, while $[Cu(CN)_3]^{2-}$ and $Cu(CN)_4]^{3-}$ do not. To minimize adsorption of copper onto activated carbon, or alternatively to elute the copper that did adsorb, free cyanide, as well as a high pH, needs to be present to ensure that the complexes are the $[Cu(CN)_3]^{2-}$ and $Cu(CN)_4]^{3-}$ oxidation states. Boshoff (1994) and Van Deventer and Liebenberg (2003) demonstrated that with low copper loadings on activated carbon, gold elution is still very good even without the cyanide pre-treatment step (cyanide free elution), but more cyanide is required to keep gold elution efficiencies high as the copper loading on the activated carbon is increased. Boshoff (1994) concluded that the success or failure of cyanide-free elutions is largely dependent on the extent of copper loading and practically independent of the amount of gold on the carbon. When the amount of copper on the carbon is low, the gold will efficiently elute, but as the copper increases, the ratio of $[Cu(CN)_2]^-$ to $[Cu(CN)_3]^{2-}$ also increases and locks the gold onto the carbon preventing efficient gold elution. Cyanide in a pre-treatment step is therefore required to convert the strongly adsorbed $Cu(CN)_2]^-$

complex to the less strongly adsorbed $[Cu(CN)_3]^{2-}$ and $Cu(CN)_4]^{3-}$ complexes and with the elution of these copper species, the gold elution increases as well.



a



b

Figure 2.5: Copper cyanide species at 25°C, pH 10.5, ionic strength ≈ 1 and 0.008 mol/L Cu for a) ideal and b) non ideal systems (redrawn from Souza et al. 2014)

The low adsorbing $[Cu(CN)_4]^{3-}$ retains a tetrahedral structure (Lu et al. 2002, Vorob'ev-Desyatovskii et al. 2012). Lu et al. (2002) describe the $[Cu(CN)_3]^{2-}$ as distorted tetrahedral, rather than a plane triangular, while Vorob'ev-Desyatovskii et al. (2002) describe it as distorted planar. The strong adsorbing $[Cu(CN)_2]^{-}$ complex is linear. (Vorob'ev-Desyatovskii et al. 2002)

Equilibrium studies by Dai et al. (2010) generally showed that the copper equilibrium loading decreases with an increasing cyanide-to-copper ratio. At low cyanide-to-copper ratios, (2.5 and 3), the equilibrium loadings closely follow a straight line on a logarithmic scale; whilst for higher cyanide: copper ratios, they do not. In particular, at the cyanide to copper ratios of 5:1 and 10:1, the copper loading shows a maximum, and decreases at high equilibrium solution copper concentrations. This was related to the increasing free cyanide concentration with increasing copper concentration. For the low cyanide-to-copper ratios of 2.5 and 3, the equilibrium loading on the activated carbon was found to be approximately 8000 g/t and 6000 g/t at 10 mg/L of Cu and would steadily increase to being close to an 100000 g/t and approximately 30000 to 40000 g/t at a 1000 mg/L Cu in the solution. Ultimately Freundlich isotherm constants were calculated for the individual $[Cu(CN)_2]^-$ (A = 2200 and n = 0.55) and $[Cu(CN)_3]^{2-}$ (A = 1500 and n = 0.4) and is shown in Figure 2.6.

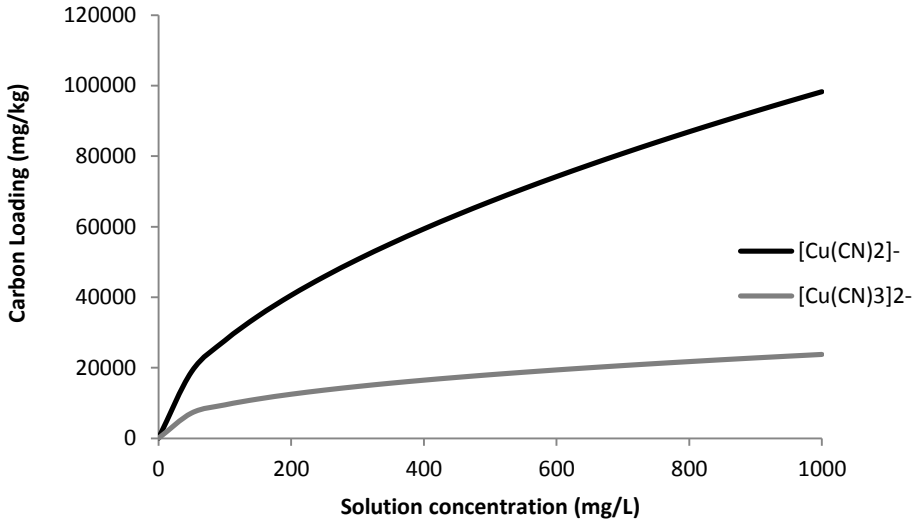


Figure 2.6: Isotherms for $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ redrawn from Dai et al. (2010).

2.7.2 Gold

Three gold-cyanide complexes are reported in literature. For gold(I) two complexes are reported:

1. The linear (Van Deventer and Van der Merwe, 1993, Vorob'ev-Desyatovskii et al. 2002) cyano anion $[Au(CN)_2]^-$ which forms the basis of the cyanide process for the extraction of gold (Sharpe, 1976, Adams et al. 1992) and
2. AuCN, which was reported by Van Deventer et al. (1994), McDougall et al. (1980), Tsuida and Muir (1986), Cook et al. (1989) and Cook et al. (1990) as an irreversible adsorbed specie (a specie that does not elute with the normal elution processes).

According to Puddephatt (1978) there is no evidence for the formation of species with a higher coordination number similar to those of copper ($[Cu(CN)_4]^{3-}$) and silver ($[Ag(CN)_4]^{3-}$) and no recent literature could be found suggesting otherwise. A potassium or sodium salt $K[Au(CN)_2]$ or

$Na[Au(CN)_2]$ can be formed by dissolving the gold powder in KCN or NaCN solution in the presence of air. On boiling an aqueous solution of these salts with 2M HCl will decompose to a lemon yellow AuCN crystal (Puddephatt, 1978). The potassium salt, $K[Au(CN)_2]$, is colourless diamagnetic crystal which is stable up to 200°C (Sharpe, 1976).

The only un-substituted cyanide anion of gold(III) appears to be $[Au(CN)_4]^-$ (Sharpe, 1976). Although not normally present in gold plant leach liquors, studies into the mechanism of the adsorption process showed that $[Au(CN)_4]^-$ also adsorbs onto activated carbon and in a similar manner to that postulated for $[Au(CN)_2]^-$. Opposed to the examples of copper, silver and gold in comparison to platinum and palladium, it was also found that the affinity of carbon for $[Au(CN)_4]^-$ which has a planar structure (Shorrock et al. 2003), is greater than that for the linear $[Au(CN)_2]^-$ (Adams et al. 1992)

According to Adams et al. (1995) aurocyanide does not convert to metallic gold up to temperatures of 240°C and is still slow at 300°C. At 300°C only 50% of the gold has become metallic and appears to involve mainly the $Au(CN)_2^-$ specie and not the stable AuCN, which readlily starts forming at low temperatures especially under acidic conditions.

2.7.3 Palladium

Sharpe (1976) describes the oxidation states attained by palladium and platinum as an interesting picture. Compared to gold, cyanide complexes for platinum and palladium (0, I, II and IV) are described. Palladium(0) and platinum(0) are each represented only by a single complex, $K_4[Pd(CN)_4]$ and $K_4[Pt(CN)_4]$. Palladium(I) and platinum(I) are stated to probably form cyano complexes, but have not been characterized yet and palladium(II) and platinum(II) cyano complexes are reported to be well known. Palladium(IV) and platinum(IV) have also been reported. Sharpe (1976), also states that platinum also forms a well defined series of solid salts in which its average oxidation state is intermediate between II and IV.

According to Monlien et al. (2002) the tetracyanopalladate(II) is a very stable complex in an aqueous solution. Even with high stability, Hancock and Evers (1976) found that in dilute HCl solutions (less than 2M), small quantities of $Pd(CN)_2$ start precipitating from a solution of $Pd(CN)_4^{2-}$ The following reaction is given:

$$Pd(CN)_{2(s)} + 2CN^- = Pd(CN)_{4(aq)}^{2-} \qquad (2.13)$$

The $Pd(CN)_2$ compound is rather insoluble in water with a solubility product of log K_{sp} = -42.

The $[Pd(CN)_4]^{2-}$ ion is planar (Sharpe, 1976)

Thermal decomposition or thermal hydrolysis of a pregnant cyanide solution is mentioned by several authors (Chen and Huang, 2006, Roijals et al. 1996, Kuzcynski et al. 1992, Desmond et al. 1991) where the metal cyanide solution is heated destroying the residual cyanide and precipitating the PGMs. The Pd-cyanide complex appears to be the least stable as the Pd in solutions starts rapidly decreasing at 160°C during the leaching of PGMs in a autoclave with the decomposition of

the $[Pd(CN)_4]^{2-}$ complex to Pd metal. $[Pt(CN)_4]^{2-}$ and $[Rh(CN)_6]^{3-}$ remain relatively stable at 160°C and only start decomposing at higher temperatures. For higher oxygen partial pressures, the rate of decomposition of the cyanide complexes increases. The thermal decomposition reaction of Pd is:

$$Pd(CN)_4{}^{2-} + \frac{3}{2}O_2 + 7H_2O = Pd + 4NH_3 + 4C0_2 + 2OH^- \quad (2.14)$$

2.7.4 Platinum

The similarity in the chemistry of platinum- and palladium containing cyanide melts suggests that platinum closely follows the behaviour of palladium. (De Haas and Fouche, 1977). Platinum–cyano complexes similar to those of palladium are formed, as already mentioned in the introduction in the above section. It is, however, stated by Sharpe (1976) as an addition to the possible platinum(0,I,II and IV) complexes formed, platinum also forms a well defined series of solid salts in which its average oxidation state is intermediate between II and IV.

Like the $[Pd(CN)_4]^{2-}$ ion, the $[Pt(CN)_4]^{2-}$ ion is planar (Sharpe, 1976)

As previously mentioned $[Pt(CN)_4]^{2-}$ remains relatively stable at 160°C and only starts decomposing at higher temperatures. (Chen and Huang, 2006, Roijals et al. 1996, Kuzcynski et al. 1992, Desmond et al. 1991) and similar to the behaviour of Pd, an increase in the rate of decomposition occurs at higher oxygen partial pressures. The thermal decomposition reaction of Pt is:

$$Pt(CN)_4{}^{2-} + \frac{3}{2}O_2 + 7H_2O = Pt + 4NH_3 + 4C0_2 + 2OH^- \quad (2.15)$$

Kuzcynski et al. (1992) and Desmond et al. (1991) found that at 225°C at a pressure of 350 psig (25 bar) 30% of Pt precipitated. Increasing the temperature to 275°C precipitated 99.8% of the Pt. Pt-cyanide complexes proved to be more stable than Rh- cyanide at higher temperatures. The final solid concentrate was a fine black powder of agglomerated particles of less than 1 μm in size containing 70% metallic PGM.

An interesting difference between Pt and Pd was found by Schoeman et al. (2012), who studied the adsorption and elution of Pt and Pd cyanide complexes onto commercially available ion exchange resins. Approximately 100% of both Pt and Pd was eluted after 15 BV with approximately similar kinetics from the resins when using potassium thiocyanate, but when using acidic thiourea as eluting agent, between 95% and 100% of the Pd could be eluted, while there was no elution of Pt cyanide. The reason for this was ascribed to the $[Pd(CN)_4]^{2-,}$ which becomes 400 times more reactive than $[Pt(CN)_4]^{2-}$ because of the formation of $[Pd(CN)^3HCN]^-$ (Schoeman, 2012, Monlien et al. 2002)

2.7.5 Nickel

The presence of significant amounts of nickel in gold ores will also have a measurable effect on all unit operations of the CIP/CIL process and result in a similar negative impact on the process as

when significant quantities of copper are present according to Fisher and LaBrooy (1997). As in the case of copper minerals, the extent of the problem will depend on quantity and the reactivity of the minerals present in the ore. The primary cyanide complex forming is the square-planar nickel(II) tetracyano complex, $[Ni(CN)_4]^{2-}$ (Vorob'ev-Desyatovskii et al. 2012).

Specifically related to the adsorption section, nickel has also been found to reduce the gold loading capacity of the activated carbon. (Fisher and LaBrooy, 1997, Sceresini and Stephen, 1992) The general preference of adsorption onto activated carbon is higher for gold and silver than for nickel, but as the quantity of nickel in the leach solution is often significantly higher, large quantities of the nickel adsorption occur, which decreases the gold adsorption. (Marsden and House, 2006, Eksteen et al. 2012). According to Fisher and La Brooy (1997), the degree to which the gold loading is affected depends on process parameters such as the pH, cyanide concentration, temperature and the metal concentrations. When these parameters were studied further, it was found that the nickel adsorption remained unchanged as the sodium cyanide concentration was decreased from 500 to 250mg/L. Precipitation of $Ni(CN)_2$ was found to occur as the solution pH dropped below 10 and precipitation of nickel as well as co-precipitation of gold was even found to occur at a pH above 12, therefore leaving the only stable pH region for Nickel adsorption to be from 10 to 12.

Boshoff (1994) concluded that the success or failure of cyanide-free elutions is largely dependent on the extent of copper loading and practically independent of the amount of gold on the carbon. While this was the case for copper, high nickel loadings were found not to have a similar effect on gold elution and Boshoff (1994), therefore concluded that nickel does not play a significant role in governing the success of cyanide free elutions. Considering the results by Fisher and La Brooy (1997), cyanide will be required in the case of a hot acid washing step being prior to elution where $Ni(CN)_2$ precipitate occurs, which blocks the pores and prevents complete gold elution.

A method, that does have a significant effect on nickel adsorption, is the acid washing step, and although not primarily its purpose, is used on industrial plants for decreasing the nickel content on the carbon according to Fisher and LaBrooy (1997). A more detailed discussion of the effects of the acid washing step was given in section 2.5.3.

2.7.6 Mercury

Mercury, when present, can be an environmental hazard, since it tends to vaporize in the regeneration furnace. Adams (1991) suggests that, in a similar manner to copper and gold, the higher oxidative state of the neutral $Hg(CN)_2$ species, which exist in the form of linear molecules, (Vorob'ev-Desyatovskii et al. 2012) adsorbs strongly onto activated carbon, while the tetrahedral anion $Hg(CN)_4^{2-}$ is weakly or practically not adsorbed at all (Vorob'ev-Desyatovskii et al. 2012, Adams, 1991) and therefore more easily eluted.

Jeffrey et al. (2009) found that distilled water is not an effective eluant for mercury. Less than 60% of the mercury could be eluted compared to more than 90% elution of gold. It was also found that

the recovery of the mercury was 57% with an acid washing step, but only 41% with no acid washing step. The mechanism by which acid washing improves mercury desorption was not investigated however. A decrease in the elution recovery from 57% to 40% was also seen when the temperature was increased from 130°C to 160°C. It was hypothesised that free cyanide is required for the mercury elution and that elevated temperatures result in a decrease of the free cyanide and ultimately in a decrease in the elution recovery at the higher temperature. Free cyanide was indeed found to have a significant impact on the elution recovery of mercury. No cyanide in the pre-treatment step resulted in a 6% recovery of mercury, while cyanide concentrations of 2% and 5% resulted in recoveries of 57% and 65%. Initial elution of the mercury is relatively fast and a peak in the mercury recovery would appear towards the start of the elution, but ultimately remain incomplete (<65%). The incomplete elution was ascribed to the presence of cyanide being only present in the pre-treatment step of AARL process, and once it was flushed out of the system, the mercury elution would stop as well. The Zadra elution process at 130°C was found to lead to a higher elution recovery (76% compared to 56%) and did not tail off or reach a limit as with the AARL process. A lower temperature for the Zadra process (110°C) also led to an increase in the recovery (87%), which corresponds to Jeffrey's et al. (2009) hypothesis regarding the importance of free cyanide for efficient mercury elution and that cyanide degradation is lower at lower temperatures, which in turn lead to a higher elution recovery.

2.7.7 Silver

Silver dissolves in a cyanide solution in a similar manner to gold and with the predominant specie formed being $[Ag(CN)_2]^-$ and insoluble silver cyanide, AgCN, formed at a lower pH or in the presence of low free cyanide concentrations (Millard, 2005, Marsden and House, 2006, Zhang et al. 1997, Adams, 1992). Vorob'ev-Desyatovskii et al. (2012) state that the composition and structure of silver cyanide complexes are defined by a molar ratio of CN^- and Ag ions in solutions. When this ratio in a solution exceeds 2.2, $[Ag(CN)_3]^{2-}$ ions can exist together with $[Ag(CN)_2]^-$ anions, and at a 10-fold molar excess of cyanide the tetrahedral anion $[Ag(CN)_4]^{3-}$ can also be present. According to Jia et al. (1998) the structure of $[Ag(CN)_3]^{2-}$ is also thought to be tetrahedral due to the formation of a $Ag(CN)_3(H_2O)^{2-}$ complex in solution. As a result, at a ratio $CN^-/Ag \geq 3$ in a solution the capacity of carbon adsorbents with respect to silver noticeably decreases due to the formation of the lower adsorbing $Ag(CN)_3(H_2O)^{2-}$ and $[Ag(CN)_4]^{3-}$ complexes (Vorob'ev-Desyatovskii et al. 2012, Jia et al. 1998). At low free cyanide concentrations, the predominant $[Ag(CN)_2]^-$ complex is still adsorbed to a lesser extent than the $[Au(CN)_2]^-$ complex. (Jia et al. 1998, Millard, 2005)

As silver adsorption kinetics is slower onto activated carbon than gold, it elutes more rapidly than gold. In the presence of low silver concentrations, typically in the region of 10% of the gold level as with Witwatersrand gold ores, the elution efficiency of silver has been found to increase with an increase in the elution temperature. With high silver loadings, however, the silver elution efficiency has been found to be inversely proportional to the temperature in the range 90–130°C. Adams (1992) suggested that at significant silver loadings the lower stability of the silver cyanide complex (between 20 and 21.9 as per Table 2.2) causes the cyanide complex to decompose and either metallic silver or silver chloride (after HCl washing) to precipitate, before elution is completed.

(Adams, 1992) Even with a lower overall elution efficiency, the elution profiles for the silver that does elute, are still sharper and earlier at higher temperatures, which in turn suggest that temperature will still enhance the elution for the complexes in the elutable form. (Millard, 2005, Costello, 1988)

2.7.8 Other metal cyanide complexes

In a manner similar to Pt and Pd, the octahedral $[Rh(CN)_6]^{3-}$ will decompose at higher temperature according to the following reaction:

$$Rh(CN)_6^{3-} + \frac{9}{4}O_2 + \frac{21}{2}H_2O = Rh + 6NH_3 + 6C0_2 + 3OH^- \quad (2.16)$$

Kuzcynski et al. (1992) and Desmond et al. (1991) found that at 225°C at a pressure of 350 psig (25 bar) 60% of Rh precipitated. Increasing the temperature to 275°C precipitated 99.8% of the Rh with Rh cyanide complexes being less stable than Pt.

2.8 Summary and significance of literature review

It has been established in Chapter 1 that alternative processing options, that are less energy-intensive and are more able to deal with complex (such as Platreef), lower grade ores are in demand and there are potentially considerable technical and economic advantages to a robust hydrometallurgical processing route for PGM ores. Leaching of PGMs with cyanide has been proposed a number of times as a promising PGM process option and progress into the understanding of cyanide leaching of PGM containing ore and concentrate has been made. The adsorption of the PGM cyanide complexes onto activated carbon has received some attention (Mpinga, 2012, Aguilar et al. 1997, Roijals et al. 1996, Desmond et al. 1991) and seems to be a feasible option. The elution thereof has been in question based on evidence, which suggests that PGMs adsorbed on carbon from a chloride solution matrix reduce to the metallic state (Milbourne et al. 2003, Fu et al. 1995, Chen et al. 2007 and Simanova et al. 2008). As elution is one of the principal unit processes in the gold carbon adsorption process, this step is deemed critical for the effective development of activated carbon process route for the Pt and Pd industry.

In order to develop a suitable process for the adsorption and elution of PGMs using activated carbon, it is imperative to understand each of the different sections of the analogous gold CIP/CIL/CIS process, which has been studied extensively and has become well established since the 1980s. Analysis of the reactions involved, stabilities and geometries of the formed complexes and adsorption and elution capabilities of associated metals are included as a means of obtaining insight into the mechanism of adsorption and elution of platinum and palladium cyanide complexes onto carbon.

Gold reacts with cyanide according to the Elsener equation and forms a stable $[Au(CN)_2]^-$ complex. PGM cyanidation occurs in the same manner as that of gold and forms stable platinum(II) and palladium(II) complexes with cyanide, namely $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$. PGM mineralogy is

complex with a significant amount of primary base metal minerals such as chalcopyrite ($CuFeS_2$), pendlandite ($(Fe,Ni)_9S_8$), and pyrrhotite ($Fe_{(1-x)}S$, x = 0 – 0.2) which will react with cyanide and affectthe adsorption and elution process.

Adsorption of platinum, palladium and gold from a solution with low concentrations of PGMs (Pt – 0.15 mg/L, Pd – 0.38 mg/L, Au, 0.1mg/L) are acceptable and the parameters, that affect this adsorption have discussed and include the type activated carbon used, temperature, oxygen, pH, associated base metals and cyanide concentration. The affinity of activated carbon for metal ions follows the selectivity sequence:

$$Au(CN)_2^- > Pt(CN)_4^{2-} > Pd(CN)_4^{2-} > Ni(CN)_4^{2-} > Cu(CN)_3^{2-}$$

Adsorption of gold predominantly takes place at the external surface of the carbon particles. The initial adsorption rate is therefore fast and determined by the diffusion of gold cyanide through the hydrodynamic boundary layer surrounding the carbon particle (film diffusion) to the external surface. When saturation of the external surface is approached, surface diffusion of the gold particles into the centre of the carbon particle becomes the rate limiting step and adsorption slows down significantly. Saturation of the external surface, however, only seems to occur at very high gold loadings (25000 mg/kg).

Some disagreement among authors regarding the mechanism of gold adsorption exists. The most widely accepted theories simplified are:

1. Adsorption involving ion pairs, $M^{n+}[\ Au(CN)_2^-]_n$.
2. Adsorption of unpaired $[Au(CN)_2]^-$ ions onto activated carbons.
3. Decomposition to other species such as AuCN, Au or a partially reduced state.

All of the above mechanisms have been shown to occur and operate under various conditions of ionic strength, pH value, and oxygen concentration. Between the adsorption mechanisms of $M^{n+}[Au(CN)_2^-]_n$ and adsorption at cationic sites on the carbon surface by ion exchange, the ion pair adsorption of $M^{n+}[Au(CN)_2^-]_n$ is the favoured one, especially at typical CIP conditions (pH ≈ 11 and T ≈ 25°C). The nature of the adsorbed species on the activated carbon and specifically whether degradation from $Au(CN)_2^-$ to AuCN occurs, remains a discussion point especially. Van Deventer and Van der Merwe (1993) ascribed these different results from different authors to the different samples of activated carbon used, since they found that different batches of carbon have different tendencies of converting $Au(CN)_2^-$ to an irreversible adsorbed AuCN which may not effect adsorption but will definitely dictate the requirement of NaCN in the elution step.

It is generally agreed that the adsorption process is a thermodynamically reversible process and that the chemical and the physical factors, that inhibit the adsorption, will enhance the elution and vice versa. The most important of these factors are temperature, cyanide and hydroxide concentrations, the ionic strength of the eluant and the acid washing step. Additional factors such as the design of the elution column, initial concentrations, column pressure and the effect of impurities were also examined and discussed.

Additional metal cyanide complexes and their reaction with cyanide and on activated carbon have been discussed individually and included for further insight in Pt and Pd behaviour, but also to determine how their presence will affect Pt and Pd adsorption and elution. In general, metal cyanide complexes are negatively charged ionic complexes consisting of one or more cyanide ions (CN–) bound to a single transition metal cation with a general formula $[M(CN)_b]^{x-}$. The complex, stability and shape of some of metal cyanide complexes are shown. Vorob'ev-Desyatovskii et al. (2012) suggested that a strong contribution to this difference in adsorption between metal cyanide complexes is attributed to the geometry of the complex. Stated in a simplified manner, linear complexes ($[M(CN)_2]^-$) adsorb strongly onto activated carbon, while planar complexes ($[M(CN)_4]^{2-}$) adsorb to a lesser extent and octahedral complexes ($[M(CN)_6]^{3-}$) do not adsorb onto activated carbon.

From the literature review is can thus be concluded that some progress, predominantly by Mpinga et al. (2014), has been made into the investigation of PGM (platinum group metals; Pt, Pd, Au) adsorption onto activated carbon at room temperature. No adsorption isotherm data exist, which would give an indication of the capacity of activated carbon for Pt and Pd cyanide complexes. In addition, as typically higher than ambient temperatures (>55°C) are likely for the leaching of Pt and Pd, it is an important factor in the adsorption process of which the effect is still largely unknown.

The mineralogy of PGMs is complex with a large number of sulfides, arsenides, tellurides and alloys. The primary base metal minerals are chalcopyrite, pendlandite, and pyrrhotite with nickel and copper grades of up to 0.3% and 0.2% in the Platreef ores (Cramer, 2001) and it is very likely that higher cyanide concentrations, as compared to gold leaching, will be required for platinum and palladium leaching (Mwase et al, 2012). Although cyanide concentration, as well as BM (Base Metal, Cu and Ni) adsorption, was investigated by Mpinga et al. (2014) the research basically only extended to one adsorption onto virgin activated carbon, which ultimately resulted in low metal loadings (≈100 mg/kg Pt, 100 mg/kg Pd and 20 mg/kg Au). Typical industrial practice, however, involves continuous loading up to a carbon loading, which would make the elution stage economical and result in the upgrading of the PGMs to a concentration that would be viable for recovery to metal. As such, the important parameters such as cyanide concentration and BM adsorption also need to be investigated under continuous adsorption conditions. Researching the influence of cyanide on the adsorption process, as well as understanding the affect of the co-adsorption of BMs under continuous conditions (experimentally executed by consecutively loading fresh solutions onto the same activated carbon) was therefore deemed important.

Fundamental research regarding an elution process for Pt and Pd is lacking. In an overview of the use of hydrometallurgy for the direct processing of PGM concentrates, Milbourne et al. (2003) stated that for the well proven gold recovery process, the carbon is readily strippable and can be recycled many times. PGMs, however, may not be as easily recovered in a stripping process, as evidence suggests that PGMs adsorbed on carbon from a chloride solution matrix reduce to the metallic state. First of all, it needs to be proven that Pt and Pd can effectively be stripped from activated carbon in a manner that would be amenable for an industrial process.

The feasibility of eluting platinum and palladium cyanide complexes from activated carbon using an analogue of the AARL process will be investigated, as well as the most important factors affecting this process. These factors are: temperature, cyanide and hydroxide concentrations and the ionic strength of the eluant. The acid washing step and the extent to which PGMs will desorb in an acid washing step will also be investigated. Factors such as the carbon loading will provide information on the upgrading potential of PGMs via a carbon adsorption process and the effect of impurities such as BMs and KSCN also needs to be considered, as these may affect the elution process deleteriously. Lastly it will be important to know in which process stream the PGMs will end up in, to ensure no PGMs losses occur with a stream being discarded in an industrial process. Knowledge of where the PGMs report to will also assist in future development of a flow sheet as well as enable the associated mass balance calculation.

Chapter 3

Materials and Method

The purpose of Chapter 3 is to discuss the materials, materials preparation and analytical techniques used. Following on from the previous chapters, the experiments were designed to investigate the adsorption and elution of Pt and Pd cyanide complexes using activated carbon. The adsorption experiments will investigate single component equilibrium isotherms for Pt and Pd followed by the effect of temperature, cyanide concentration and BMs (Cu and Ni) on the adsorption of the PGMs under consecutive loading conditions, which are more reflective of industrial plant conditions than just one single adsorption stage. The elution of Pt and Pd will be investigated through an analogue of the AARL process including several of the factors expecting to affect this process. The different experimental procedures are described and their relevance discussed. Concentrations and conditions chosen for each of the experiments are shown and discussed. The repeatability of the experiments is also discussed in this chapter.

3.1 Materials and preparation of materials

3.1.1 Activated carbon

A coconut-based granular activated carbon, supplied by Marlyn chemicals (Pty) Ltd-South Africa, with a BET surface area of 1200 m^2/g and iodine number 1075 mg/g according to the specifications of the supplier, was used for the adsorption and elution experimentation work. Additional supplier specifications for the activated carbon can be seen in Appendix A. Prior to use, the adsorbent was washed with hydrochloric acid (5%) at 25°C and subsequently dried at 80°C for 48 hours. The water-washing was stopped when the pH value of the suspension remained constant at 7. This operation significantly reduced the amount of superficial mineral impurities and powder (ash) and the XRF analysis of the carbon before and after this operation can be seen in Table A.34 in Appendix A. The activated carbon was sieved to obtain a particle size fraction between 1180 and 3350 µm, with a d_{50} grain size of 2360 µm for all the experiments (Mpinga, 2012).

3.1.2 Adsorbates

It has been shown that PGM cyanidation occurs in the same manner as that of gold and that the reactions follow the Elsener equation to form stable complexes with cyanide, namely $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ (Mwase et al. 2012, McInnes et al. 1994, Hancock et al. 1977, Chen and Huang, 2006). If the PGMs are in a sulphide complex (PtS or PdS) it will still form the same complexes with cyanide as in the case of the Elsener equation. Synthetic solutions could therefore be made up by dissolving $K_2Pd(CN)_4.H_2O$ (99%, Sigma-Aldrich), $K_2Pt(CN)_4.H_2O$ (98%, Sigma-Aldrich) and $KAu(CN)_2$ (99%, Sigma-Aldrich) to the required amounts in distilled water. Unless otherwise stated, solutions were buffered to a pH of 9.5 by adding $NaHCO_3$ and Na_2CO_3 in the mol ratio of

[1:5.6]. Base metals, where required, were added as $K_2Ni(CN)_4$ (Sigma-Aldrich) and CuCN (99%, Sigma-Aldrich). All other chemicals were of analytical grade. Where required, powdered NaCN (98%, Kimix), KSCN (Sigma-Aldrich) and NaOH (Sigma-Aldrich) were added.

3.2 Adsorption experiments

Two different methods were employed for the adsorption of the metal cyanide complexes onto the activated carbon: (Details to follow in the description of each experiment)

1. The bottle-on-rolls method - Single component isotherm development and carbon loading for elution.
2. Stirred vessels - Kinetic rate and continuous adsorption experiments

It should be taken into consideration that the mass transfer kinetics of the stirred vessels will be different than with the bottle-on-rolls method. Fleming et al. (2011) demonstrated that the mixing is more efficient in a stirred vessel than with the bottle roller tests and this translates to improved adsorption performance. To put these two different tests into perspective, Fleming et al. (2011), related the kinetic performance, that was achieved in large conventional CIP tanks, to be similar to that of a rolling bottle, while the performance of smaller, well-mixed tanks such as Pumpcells, to be better simulated by small laboratory stirred tanks.

3.2.1 Development of the Isotherms

The single component equilibrium isotherms were determined by contacting weighed samples of between 0.6 and 4 g/L activated carbon with 500mL of platinum and palladium synthetic solutions of 30 and 70 mg/L at room temperature and a pH of 9.5 (Table 3.3), by means of the bottle-on-rolls method for 72 hours in 1 L bottles (Van der Merwe, 1991) at the rotational rate of 105 rpm. The rate of loading of gold cyanide onto carbon in a rolling bottle test is insensitive to the rate at which the bottle is rolled as long as the inside of the bottle is smooth and without baffles (Fleming et al. 2011). Liebenberg and Van der Merwe (1997) deemed a pseudo equilibrium time of 72 hours as effective for the fundamental modelling of gold CIP/CIL circuits, although true gold adsorption equilibrium will take more than three weeks to reach. As a Pt and Pd adsorption test from a solution containing approximately 30mg/L of Pt and Pd and 5mg/L of Au showed equilibrium for Pt and Pd was obtained after 47 hours already (Figure A.1 in Appendix A), 72 hours were also deemed an appropriate contact time to determine the Pt and Pd isotherms.

High PGM concentrations of 30 and 70 mg/L for the base solutions were chosen to ensure equilibrium between the solution and the loading on the activated carbon was reached instead of just 100% adsorption onto the activated carbon. The base concentration of 64 mg/L for palladium instead of 70 mg/L was used, as the solution had already been made as base solution from previous experiments and was deemed adequate for the isotherm determination.

Table 3.3: Base concentrations for the development of single component isotherms for Pt and Pd

AC Concentration (g/L)	Pt concentration (mg/L)	Pd concentration (mg/L)	volume (mL)	pH
4	30	30	500	9.5
3	30	30	500	9.5
2	30	30	500	9.5
1	30	30	500	9.5
0.6	30	30	500	9.5
4	70	64	500	9.5
3	70	64	500	9.5
2	70	64	500	9.5
1	70	64	500	9.5
0.6	70	64	500	9.5

3.2.2 Temperature loading experiments

Two sets of experiments are described in this section:

1. Initial adsorption experiments to determine the effect of temperature on the kinetics of adsorption
2. Consecutive loading experiments to investigate the combined effect of temperature, cyanide and base metals.

For both of the procedures, the synthetic solution containing the mixed metal cyanides was divided into volumetric flasks, which were submerged into a water bath set at the desired temperature (25, 35 and 50°C). Once the 500mL synthetic solution reached the required temperature, it was emptied into a 1 L beaker (also submerged in the heated water bath and kept in place) with 10 g/L of activated carbon and agitated with a coated axial flow impeller type stirrer. The stirrer was set to 650 rpm at a fixed position, that would be used for all experiments. The temperature of the solution was measured throughout the duration of the experiments, which remained constant at the set temperature.

To determine the kinetics of adsorption with temperature, samples were taken at 0, 0.25, 0.5, 1.0, 1.5, 2.0 and 3.0 h with initial concentrations as indicated in Table 3.4. Initial concentrations were selected to compare with the adsorption results obtained by Mpinga (2012), which in turn were selected on the basis of a cyanide heap leach process for Platreef ores (Mwase et al. 2014). An analysis of the leach solution as obtained from Mwase et al. 2014 can be seen in

Table A.35 in Appendix A. Samples (5 mL) were filtered using a 0.45 µm syringe filter to remove any carbon fines that might be present in the solution before analyses of the filtrate by ICP-MS. The uptake of metals onto the activated carbon was determined from the difference of metal concentrations in the initial and sampled solutions as per Eq. 3.1 where C_0 is the initial solution concentration and $C_{i,t}$ the sample concentration at time (t).

$$Adsorption_{i,t} = \frac{C_0 - C_{i,t}}{C_0} \quad (3.1)$$

Table 3.4: Experimental conditions for determining the effect of temperature on the kinetics of adsorption of Pt, Pd and Au cyanide complexes

Nr	Temperature (°C)	Activated carbon concentration (g/L)	Pt Concentration (mg/L)	Pd Concentration (mg/L)	Au Concentration (mg/L)	Volume (mL)	pH
1	25	10	0.9	1.0	0.2	500	9.5
2	35	10	0.9	1.0	0.2	500	9.5
3	50	10	0.9	1.0	0.2	500	9.5

For the consecutive loading test, 500 ml of the synthetic solution (Table 3.5) was mixed with 10 g/L of activated carbon as described above. The solution was sampled after two hours of adsorption, and the remaining synthetic solution was split from the activated carbon by filtering using a Buchner funnel. The test was repeated four times using the already loaded activated carbon and a fresh synthetic solution. As per the previous test, samples (5 mL) were filtered using a 0.45 µm syringe filter to remove any carbon fines that might be present in the solution before analyses of the filtrate by ICP-MS. The total adsorption of metals onto the activated carbon for the four loadings was determined from the difference of metal concentrations in the initial and sampled solutions for all four loadings as per Eq. 3.2, where C_0 is the initial solution concentration and $C_{i,2}$ the sample concentration after two hours.

$$Total\ Adsorption = \frac{(C_0 - C_{i,2})_{loading1} + (C_0 - C_{i,2})_{loading2} + (C_0 - C_{i,2})_{loading3} + (C_0 - C_{i,2})_{loading4}}{4C_0} \quad (3.2)$$

Mineral impurities that were considered for this study included Cu, Fe and Ni which were found in significant quantities in the experimental heap leach solution as per Table A.35. Fe does not adsorb onto activated carbon (Mpinga, 2012) while Cu and Ni co-adsorb and is well known to cause problems in Au carbon adsorption plants. Other impurities such as Pb are only available in trace amounts while Mn was below the instrument detection limit. A pH of 9.5 was chosen for all

adsorption experiments. Fleming and Nicol (1984) and McDougal et al. (1980) found that a lower pH favours adsorption. Plant operations are, however, limited in the pH where the plant can safely be operated at due to the formation of toxic HCN when the pH of the solution is decreased. A pH of 9.5 will therefore allow for maximum PGM adsorption while being on the limit of what would be considered as safe plant operation. Mpinga (2012) also indicated higher PGM adsorption at a pH of 9.5 with adsorption slightly decreasing by approximately 2 percentage points (pp) as the pH was increased to 12.

Table 3.5: Experimental conditions for determining the effect of temperature, cyanide and BMs on the consequtive adsorption of Pt, Pd and Au cyanide complexes

			BM Concentration (mg/L)		PGM concentration (mg/L)		
Nr	Temperature (°C)	Cyanide Concentration (mg/L)	Ni	Cu	Pt Concentration (mg/L)	Pd Concentration (mg/L)	Au Concentration (mg/L)
1	25	0	0	0	0.9	1.0	0.2
2	50	0	10	10	0.9	1.0	0.2
3	25	0	10	10	0.9	1.0	0.2
4	50	0	0	0	0.9	1.0	0.2
5	25	300	10	10	0.9	1.0	0.2
6	50	300	0	0	0.9	1.0	0.2
7	25	300	0	0	0.9	1.0	0.2
8	50	300	10	10	0.9	1.0	0.2

The consecutive loading tests were adapted from the Pica procedure (Staunton, 2005) where a sample of carbon was contacted for 1 hour with 1 L of 10 mg/L gold solution. The carbon was recovered and put into a fresh batch solution for a further hour and repeated for a number of times. The one hour can be related to the residence time of the aurocyanide complex of approximately 1 h in each tank on an industrial adsorption plant (Stange, 1999). The cumulative gold loading after each contact was calculated and the data points were plotted to show the increase in the gold loading on the carbon with increasing number of solution contacts, as well as the extraction per stage for interest in the development of an industrial process. In this case, two hours were chosen based on findings by Mpinga et al. (2014), who found that Pt and Pd extraction after two hours were high (>90%) while Cu extraction was low (<20%) .

3.2.3 Loading for elution

Loading of the activated carbon was achieved by contacting the synthetic solutions with the activated carbon by means of the bottle-on-rolls method at 105 rpm. The synthetic solutions were made up as per Table 3.6 with the majority of the experiments being conducted with an initial concentration of 5 mg/L of Pt, Pd and Au each. Contacting with the activated carbon occurred for approximately 65 hours resulting in a PGM loading of approximately 650 g/t of Pt, Pd and Au each. Typical industrial scale Au loading on activated carbon before elution ranges from 300 to 7000 g/t. Boshoff (1994) also suggested the elution efficiency to be rather independent of the amount of gold present on the activated carbon, and it was therefore deemed appropriate to select a low, but convenient and easily detectable loading for this study. Equal amounts of gold, platinum and palladium were chosen for easy comparison between the known gold elution ability, for which a significant amount of research had been completed, and the unknown platinum and palladium elution ability. The validity of this assumption was, however, tested by increasing the initial concentration of Pt and Pd to 30 mg/L followed by an elution step as indicated in Table 3.6 nr 4. The analysis of the actual concentrations for each of the experiments is given in Appendix B.

Table 3.6: Activated carbon loading for corresponding elution experiments (All loadings buffered to pH 9.5 at room temperature)

	Synthetic solution concentration for carbon loading (mg/L)								
Nr	Pt	Pd	Au	Cu	Ni	SCN	CN^-	Time (hr)	Elution Experiment
1*	5	5	5	0	0	0	0	65	A - E, H, K - Z, AA - AE, AI - AH
2	5	5	5	50	0	0	30	65	F - G
3	5	5	5	50	0	100	30	65	I - J
4	30	30	5	0	0	0	0	120	High
5	0	0	10	0	0	0	0	65	AL - AM
6	5	5	5	100	100	0	100	65	ACID 1 - 5

* loading procedure nr 1 does not represent just one loading but the conditions for several different loadings

3.3 Elution experiments

The method for the elution experiments as described by Van Deventer et al. (1994) was followed. The majority of the elution investigative runs were conducted with the loaded carbon in a glass column with a temperature controlled water jacket. The aim of this study was to investigate the possibility of elution of Pt and Pd and not to obtain the highest possible elution efficiencies. Therefore, a convenient temperature of 80°C was selected for most of the elution runs, except for the elution runs where the effect of temperature was specifically investigated. For these runs, the jacketed glass column (12 mm diameter with a total length of 270 mm) was used for eluant temperatures below 100°C. The dimensions of the column correspond to the 12 mm diameter gold elution columns with 9g of activated carbon used by Van Deventer and Van der Merwe (1990), Van der Merwe and Van Deventer (1990) and Van Deventer and Van der Merwe (1994), as well as to Banini and Stange (1994), who didn't specify their column dimensions, but eluted 15g of carbon for each of their experiments to which models were fitted. For elution runs above 100°C, a stainless steel pressurised column was used with a detailed description of the pressurized column to follow in section 3.3.1. The flow of eluant through both of the columns was controlled by manual adjustment of the outlet valve. A bed volume (BV) is defined here as the empty volume of the

column, that is occupied by the packed bed of carbon and was calculated for each experiment, but since equal amounts of AC were used for each experiment (12 g, wet), the BV did not change.

The pre-treatment step was conducted outside the column by stirring the activated carbon in glass beakers for 30 min in 40 mL of water treated through a reverse osmosis (RO) plant (Table A.38 and Table A.39 in Appendix A) with various concentrations of NaCN and NaOH at room temperature. After the pre-treatment, the carbon was separated from the solution by decanting, and the excessive solution removed by filtering. The carbon was then dropped into the glass column containing half a bed volume of eluant at the elution temperature. The starting time for the elution was taken as the moment when flow of eluant was introduced.

Photos of the adsorption and elution experimental set-up can be seen in Figure 3.7 and a schematic of the elution column in Figure 3.8

a  b 

c 

Figure 3.7: Photos taken of the a) adsorption (Mpinga, 2012), b) pre-treatment step and c) elution column

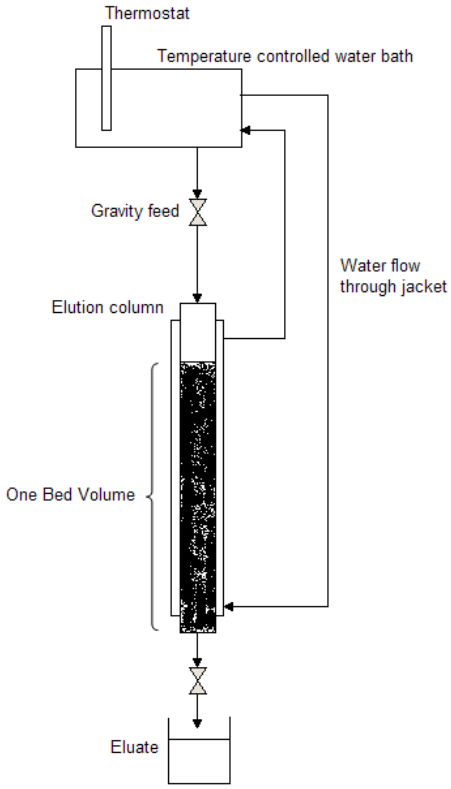


Figure 3.8: Experimental arrangement for elution in the glass column

The experimental set-up (Figure 3.9 and Figure 3.10) for the elutions above 100°C consisted of a reservoir from which water, treated through a reverse osmosis plant, was pumped through a coil of approximately 2.5 m submerged in a heated oil bath and through the elution column (38 ømm, length – 200 mm, BV – 80mL). The heated oil was pumped through the jacket of the elution column, which was also lagged for safety purposes as well as to reduce heat losses. The system was pressurised with nitrogen and kept above 3.1 bar. The solution exiting the elution column was cooled before sampling commenced.

Pre-treatment for the activated carbon in the stainless steel column was completed in a 1 L glass beaker with 210 mL of pre-treatment and 40 g AC (dry weight).

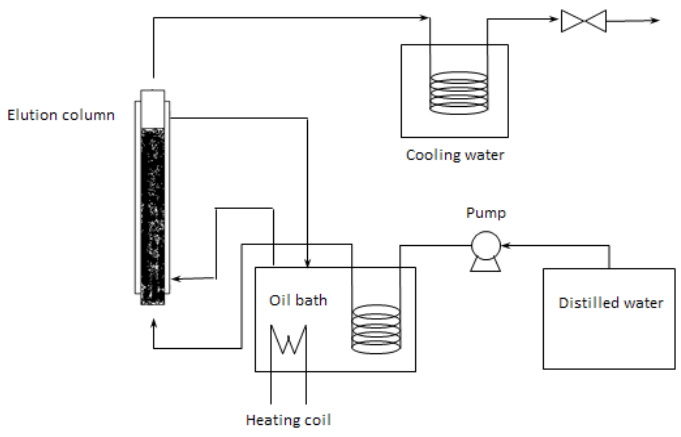


Figure 3.9: Schematic for the experimental arrangement for the high temperature elution in the stainless steel column at pressure.

Figure 3.10: Experimental arrangement for the high temperature elution in the stainless steel column at pressure.

According to Schoeman (1991) carbon concentration is a volumetric measurement and the conversion to mass is usually done by applying a factor for the bulk density of carbon. It was also stated that the bulk density of the carbon should be checked, as it can significantly vary from virgin to loaded carbon, which can significantly impact on results. For these specific experiments, a great variability in mass and volume was also found between dry, wet and adsorbed carbon. It was therefore deemed important that after adsorption, the carbon was immediately split into mass amounts of 12g to be used for the different elution experiments. After each elution experiment, the eluted carbon was dried at 80°C until the mass of the carbon did not change any longer (approximately 7 hours) and the dry weight of the activated carbon for each experiment then recorded.

From the literature review, the most important variables to be tested for the elution of PGMs from activated carbon are temperature, NaCN and NaOH concentrations in the pre-treatment step, the ionic strength of the eluant, the effect of an acid washing prior to elution as well as the impact of impurities such as copper and thiocyanate. The conditions and concentrations used for each experiment to determine the effects of these variables, are shown in the following sections.

3.3.1 Determining the effect of elution temperature

To determine the effect of temperature, experiments were conducted at:

1. 60 and 80°C in the glass elution column as per Figure 3.8
2. 100 to 130°C in a pressurised stainless steel column as per Figure 3.9 and Figure 3.10

Experimental conditions for determining the effect of temperature on the elution of PGMs is shown in Table 3.7. Both the effect of the pre-treatment temperature as well as the elution temperature was researched.

Table 3.7: Experimental conditions for determining the effect of temperature on the elution of Pt, Pd and Au.

Nr	Exp	NaOH (% wt/wt)	NaCN (% wt/wt)	Flow rate (BV/hr)	Temperature of pre-treatment (°C)	Elution temperature (°C)
1	D	0.6	0	2	25	60
2	E	0.6	2	2	25	60
3	H	0.6	2	2	25	80
4	AI	0.6	2	30	25	80
5	AH	0.6	2	2	25	95
6	T1	0.6	2	30	25	100
7	T2	0.6	2	30	25	110
8	T3	0.6	2	30	25	120
9	T5	0.6	2	30	25	130
10	T6	0.6	2	30	25	130
11	T7	0.6	2	30	80	100
12	T8	0.6	2	30	80	110
13	T9	0.6	2	30	80	120
14	T10	0.6	2	30	80	120
15	T11	0.6	2	30	80	130

3.3.2. Cyanide and hydroxide pre-treatment

As previously stated, the pre-treatment step was conducted outside the column by stirring the activated carbon in glass beakers for 30 min. in 40 mL of water with various concentrations of NaCN and NaOH at room temperature. The appropriate amount of NaOH was measured and dissolved in 40 mL of water from a reverse osmosis plant (see Table A.38 in Appenidix A). Care was taken to ensure that the NaOH was always dissolved first to ensure the pH is high enough (> 8) to prevent the formation of toxic HCN gas when the NaCN was added. All solids were visibly dissolved before the loaded activated carbon was added and stirred for 30 min. The selected concentrations for the NaCN and NaOH are shown in Table 3.8 and refer to loading procedure nr 1 as per Table 3.6.

Table 3.8: Experimental conditions for determining the effect of the NaOH and NaCN concentrations in the pre-treatment step on the elution of Pt, Pd and Au (Activated carbon loading of 650g/t of Pt, Pd and Au each, elution temperature = 80°C)

nr	Exp	NaOH (% wt/wt)*	Pre-treatment NaCN (% wt/wt)	Temperature of pre-treatment (°C)
1	M	0.3	2.0	25
2	O	0.6	0.0	25
3	Q	0.6	1.0	25
4	P	0.6	2.0	25
5	S	0.6	3.0	25

* All % by mass

6	T	0.6	4.0	25
7	U	1.1	0.0	25
8	V	1.1	1.0	25
9	W	1.1	2.0	25
10	X	1.1	3.0	25
11	AC	1.1	4.0	25
12	Z	1.7	0.0	25
13	Y	1.7	1.0	25
14	AA	1.7	2.0	25
15	AB	1.7	3.0	25
16	AD	1.7	4.0	25
17	C	2.0	0.0	25
18	B	2.0	0.3	25

Since Van Deventer and Van der Merwe (1993) found that different batches of carbon have different tendencies of converting $Au(CN)_2^-$ to AuCN, elution experiments containing only gold were conducted to determine the nature of the activated carbon and its effect on gold elution. Table 3.9 indicates the pre-treatment conditions for the 'gold only' elutions. Table 3.9 refers to loading procedure nr 5 as per Table 3.6.

Table 3.9: Experimental conditions for determining the effect of the NaOH and NaCN concentrations in the pre-treatment step on the elution of Au only. (Activated carbon loading of 650g/t of Au, elution temperature = 80°C)

		Pre-treatment		
nr	Exp	NaOH (%)	NaCN (%)	Temperature (°C)
1	AL	0.6	0.0	25
2	AM	0.6	2.0	25

3.3.3 The effect of PGM carbon loading

The validity of the assumption that the elution efficiency is independent of the amount of Pt and Pd present on the activated carbon was tested by increasing the loading on the activated carbon significantly. The experimental conditions for the elution from a highly loaded activated carbon are shown in Table 3.10 (refer to loading procedure nr 4 as per Table 3.6).

Table 3.10: Experimental conditions for determining the effect of the carbon loading on the elution of Pt and Pd (carbon loading as per Table 3.6 - loading procedure 4, elution temperature = 80°C)

		Pre-treatment		
nr	Exp	NaOH (%)	NaCN (%)	Temperature (°C)
1	High	0.6	2.0	25

3.3.4 Ionic strength of the eluant

The effect of ionic strength on the elution of Pt, Pd and Au was tested by the addition of NaCl to the eluant in the temperature controlled water bath as shown in Figure 3.8. An experiment on the effect of water quality (ionic strength) on gold elution by Davidson and Baily (1991) was used as a guideline and the selected concentrations of the Na^+ ions for these experiments can be seen in Table 3.11. Loading occurred as per procedure nr 1 in Table 3.6.

Table 3.11: Experimental conditions for determining the effect of the ionic strenght on the elution of Pt, Pd and Au. (Activated carbon loading of 650g/t of Pt, Pd and Au each, pre-treatment with 2% NaCN and 0.55% NaOH at 25°C, elution temperature = 80°C)

nr	Exp	Na^+ (mg/L)
1	AI	80
2	AJ	150
3	AG	200
4	AH	300

3.3.5 Effect of impurities

From literature (Cramer, 2001) it was found that the PGM mineralogy, as found in South Africa, is complex with a large number of sulfides, arsenides, tellurides and alloys. The primary base metal minerals are chalcopyrite ($CuFeS_2$), pendlandite ($(Fe,Ni)_9S_8$) and pyrrhotite ($Fe_{(1-x)}S$ (x = 0 to 0.2)) with nickel and copper grades of 0.2% and 0.1% found in the Merensky ore and up to 0.3% and 0.2% in the Platreef ores.

The effect of both copper and nickel on the adsorption of PGMs has been researched by Mpinga (2012) and is also researched and included in this study (section 3.2.2). Specifically relating to the elution process, the formation of the different adsorbing Cu cyanide complexes (Boshoff, 1994) has been deemed both important and interesting and the effect of Cu with varying cyanide pre-treatment concentrations was therefore specifically investigated. The effect of Ni and Cu when an acid pre-wash is performed, is also investigated. Fe, which is also present in large quantities in South African PGM ores, has been shown to adsorb to a very small degree (Mpinga, 2012, Vorob'ev-Desyatovskii et al. 2012) and the possible effect it may have on the elution of PGMs has therefore not been included in this study.

Mwase et al. (2014) found that during the initial stages (4 to 8 days) of column leach experiments, NaCN conversion to thiocyanate was high (≈35%), which gradually decreased over 32 days to between 12 and 6% (<< 100 mg/L SCN^-) depending on the ore size leached. Although Mpinga et al. (2013) found that 100 mg/L [SCN^-] concentration was not an inhibiting factor for PM adsorption, no literature could be found to suggest what the effect of thiocyanate would be on the elution of Pt and Pd specifically, and was therefore included in this investigation. The effect of thiocyanate on the elution was investigated by adding KSCN salt to the adsorption solution during elution.

The experimental conditions for the elution from activated carbon containing Cu and SCN^- are shown in Table 3.12 (refer to loading procedure nr 2 and 3 in Table 3.6).

Table 3.12: Experimental conditions for determining the effect of Cu and SCN^- on the elution of Pt, Pd and Au. (Activated carbon loading of 650g/t of Pt, Pd and Au each, elution temperature = 80°C)

				Pre-treatment		
nr	Exp	Impurity	Loading procedure	NaOH (%)	NaCN (%)	Temperature (°C)
1	F	Cu^+	2	0.6	2.0	25
2	G	Cu^+	2	0.6	0.0	25
3	I	Cu^+, SCN^-	3	0.6	0.0	25
4	J	Cu^+, SCN^-	3	0.6	2.0	25

The conditions used to study the effect of Ni and Cu when an acid pre-wash is performed are discussed in the next section.

3.3.6 The acid wash

The primary purpose of the acid washing step was to investigate whether Pt and Pd would partially or completely elute during this stage. If significant elution of any one of these metals occurs, it would certainly simplify the decision (since there is some disagreement) on where to place (before or after elution) this important step in the process.

The experiments involving the acid washing step consisted of the following sequence:

1. Stirring the loaded activated carbon with various concentrations of hydrochloric acid (HCl) for 45 min at low and high temperatures (Table 3.13).
2. A rinsing step with 100 mL of distilled water for 15 min.
3. Pre-treatment with 2% NaCN and 0.6% NaOH at 25°C .
4. Elution with RO water at 80°C.

Base metals were added as $K_2Ni(CN)_4$ (Sigma-Aldrich) and CuCN (99%, Sigma-Aldrich) and cyanide as NaCN (Sigma-Aldrich) for adsorption as per loading procedure nr 6 in Table 3.6.

Table 3.13: Experimental conditions for determining the effect an acid wash stage prior to the elution of Pt, Pd and Au. (Activated carbon loading of 650 g/t of Pt, Pd and Au each, pre-treatment with 2.0% NaCN and 0.6% NaOH at 25°C, elution temperature = 80°C)

nr	Name of Exp	HCl concentration (M)	Temperature (°C)
1	Acid 1	1	25
2	Acid 2	3	25
3	Acid 3	1	70
4	Acid 4	3	70
5*	Acid 5	0	-

*No acid washing was performed for comparison purposes.

3.4 Sampling procedure and analytical methods

During both the rolled bottle as well as the stirred adsorption experiments, the initial clear solution would turn black, due to the abrasion and breakage of the granular carbon particles and formation of activated carbon fines. For all of the adsorption experiments, 5 mL samples were taken with a pipette and filtered with a 0.45 um syringe filter to prevent any further adsorption in the sample

tubes by carbon fines before analysis. Samples were taken at time intervals as dictated by each of the experiments.

Two sampling strategies were employed during the elution experimentation:

1. Consecutive sampling for determination of the elution concentration profile
2. Bulk sampling for comparison purposes

For determination of the elution concentration profile, consecutive samples were taken at the outlet of the elution column. Since the elution kinetics of Pt and Pd was found to be rather fast and to ensure capturing of the elution concentration peak, all of the eluant was sampled for the first 3 to 4 bed volumes (first 8 samples) in 5 mL samples following immediately after one another. From the sample 6 - 8 and onwards, the time between samples were gradually increased, as the elution kinetics slowed down and the PGMs were washed out of the column. Figure 3.11 gives an example of the sampling size and rate of sampling in relation to the developed elution profile. Samples from the pre-treatment solution were taken with a pipet and analysed without filtering. Water samples prior to elution were taken through the elution column at the column outlet to ensure no contaminants inside the columns could influence the PGM elution.

For the second sampling strategy a single sample, after approximately 5 bed volumes of eluant flowed through the column, was taken where a comparison between the methods was deemed adequate. Examples of these are the determination of the effect of the ionic strength of the eluant and the acid wash experimentation. This method of sampling is less ideal as it contains less information but was deemed adequate considering the costs involved for analysis.

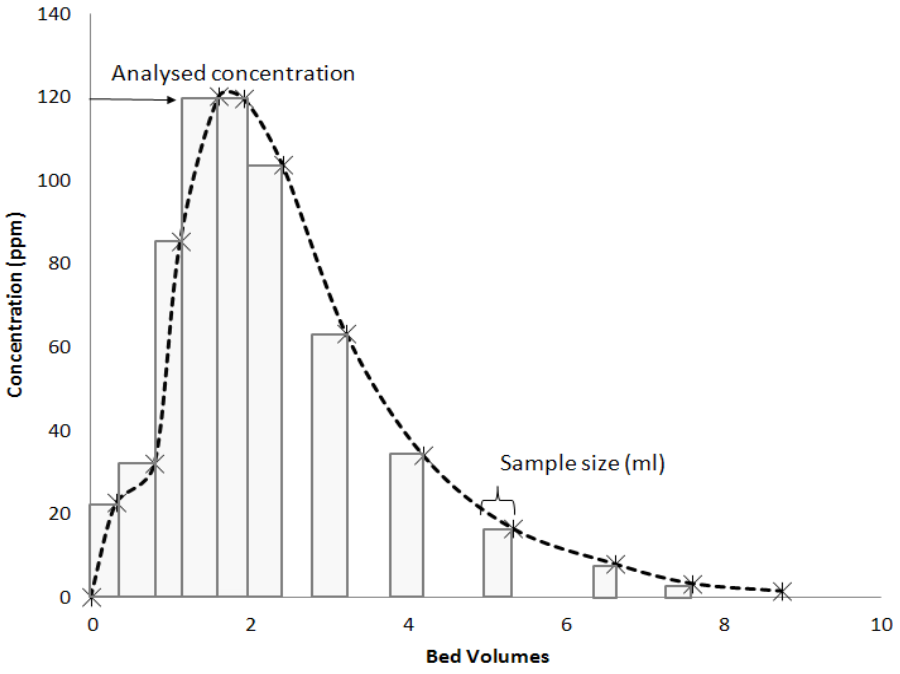


Figure 3.11: An example of the sampling size and rate of sampling in relation to the developed elution profile. The first samples follow immediately after each other to capture the concentration peak after which the time interval between samples increases as the elution progress (Sample size to scale).

For the sample analysis, either Inductively Coupled Mass Spectroscopy (ICP-MS) or Inductively Coupled Optical Emission Spectroscopy (ICP-OES) was used for determination of the metal ions in solution. The ICP-MS (detection limits <20 ppt) was predominantly used for the adsorption experiments, where the initial metals concentrations were very low (< 1 mg/L) and would get even lower as adsorption took place. ICP-OES was used for all the elution experiments as well as for the isotherm determination, where the metal concentrations were either fairly large (>1mg/L) or an accuracy of less than 1mg/L (ppb range) was less important as in the case of the PGMs eluting in the pre-treatment step

Sampling for the Steel column

A similar sampling strategy was followed for the steel elution column, but due to the larger size of the steel elution column and corresponding larger bed volumes (80 mL BV compared to 15 mL BV for the glass column), the sampling frequency was marginally different and is summarized in Figure 3.12 below.

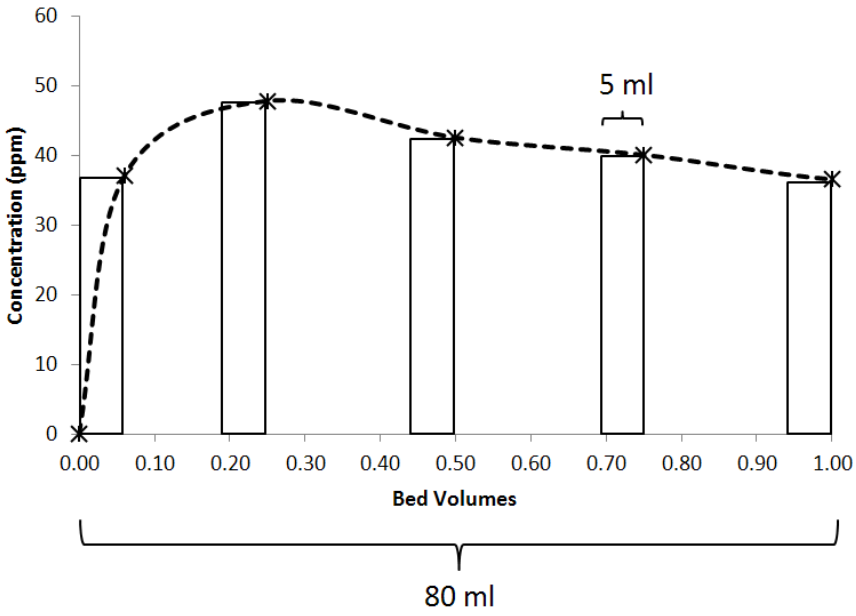


Figure 3.12: An example of the sampling size and rate of sampling in relation to the developed elution profile for the steel elution column (Sample size to scale).

Analytical methods

All samples (5 mL) were filtered using a 0.45 µm syringe filter to remove any carbon fines, that might be present in the solution before analyses of the filtrate by either a Thermo Icap 6200 Radial ICP-AES (isotherms and elution experiments) or an Agilent 7700 ICP-MS (kinetic rate and continuous adsorption experiments).

The activated carbon surface deposits were studied using a Zeiss Auriga field emission gun (FEG) SEM operated at 5 kV with an in lens detector for secondary electron imaging. For the EDS analysis, an Oxford Instruments X-Max solid-state silicon drift detector (SDD) with beam energy of

20kV was used. Sample preparation entailed placing a few granules of the loaded activated carbon on an Al stub covered with an electrically conductive graphite disc, which was then coated for 30 seconds with a iridium layer (equates to roughly 10 nm) using a Quorum Q150T metal sputter coater at a base pressure of 10-4 mbar.

For the Transmission Electron Microscopy a FEI Tecnai F20 FEG TEM operated at 200kV in bright field mode was used with a Gatan Ultrascan 1000 high CCD camera for image collection. The samples were prepared by dispersing a few mg of the powdered sample in 20 ml of ethanol. The ethanol solution was then ultrasonicated for 10 minutes to improve the dispersion of the sample in the ethanol and once completed, 10 micro litres of the solution was placed on a carbon coated Cu grid, which was then placed under a light source for 15 minutes to dry out the ethanol.

3.5 Repeatability

3.5.1 Consecutive adsorption repeatability

For the consecutive adsorption repeatability test, the experiment at 50°C, 0 mg/L NaCN and no base metals was repeated three times. Tests 1 and 2 were close to one another with a variance of 0.001 and a standard deviation of 0.03. Test 3 was completed with a different sodium bicarbonate as buffer and resulted in slightly higher adsorption. The only other run, where this sodium bicarbonate was used, was in the presence of 300 mg/L NaCN with 10 mg/L base metals at 25°C. By including test nr 3, the variance increased to 4.5 and the standard deviation to 2.1. See Figure 3.13.

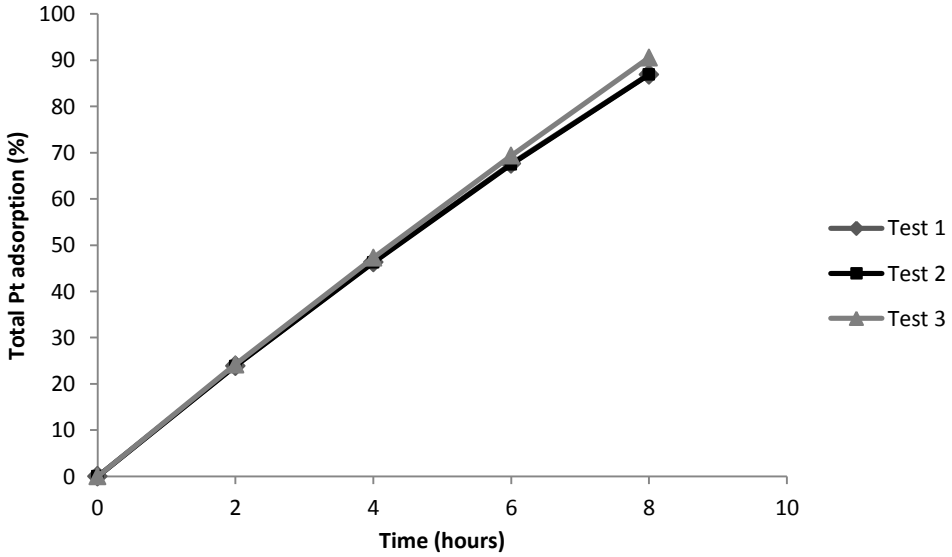


Figure 3.13: Repeatability test for consecutive Pt adsorption (T = 50°C, pH = 9.5, BM = 0, Pt = 1 mg/L, Pd = 0.15, Au = 0.22mg/L)

3.5.2 Elution repeatability

Elution experiments with 0 NaCN and 0.6% NaOH pre-treament concentrations at 80°C were repeated 6 times, of which four experiments (R1 to R4) were from the same loading experiment (Loading I). The results are shown in Table 3.14. From the repeated results, the mean, variance, standard deviation and standard uncertainty were calculated. The standard uncertainty is calculated here by Eq. (3.3), which is also often referred to as the standard error. According to the publication "Evaluation of Measurement Data — Guide to the expression of uncertainty in measurement 2008", the experimental standard deviation of the arithmetic mean or average of a series of observations, is *not* the random error of the mean, although it is often designated as such. It is rather a measure of the uncertainty of the mean due to random effects. The term 'error' is an idealized concept and the exact value of the error in the mean arising from the random effects cannot be known.

$$u = \frac{\sigma}{\sqrt{n}} \tag{3.3}$$

Table 3.14: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈650 mg/kg of Pt, Pd and Au each) at an elution temperature of 80°C.

	Pre-treatment		Recovery (%) 4 BV			Recovery (%) 5 BV			Recovery (%) 9 BV
Exp	NaOH (%)	NaCN (%)	Pd	Pt	Au	Pd	Pt	Au	Au
K	0.6	0	42	35	1.0	49	41	1.5	2.0
O	0.6	0	49	43	1.1	55	49	1.4	2.7
R 1	0.6	0	47	40	1.6	56	49	2.2	4.2
R 2	0.6	0	49	43	1.4	55	49	1.9	4.2
R 3	0.6	0	46	39	1.0	56	49	1.4	2.8
R 4	0.6	0	39	32	0.8	50	42	1.1	2.4
Mean			**45.3**	**38.7**	**1.2**	**53.5**	**46.5**	**1.6**	**3.1**
Variance			**16.3**	**19.5**	**0.1**	**9.9**	**15.1**	**0.2**	**0.9**
Stdeviation			**4.0**	**4.4**	**0.3**	**3.1**	**3.9**	**0.4**	**0.9**
Standard uncertainty			**1.6**	**1.8**	**0.1**	**1.3**	**1.6**	**0.2**	**0.4**

Differences in elution results are attributed to one or all of the following:

1. Analytical errors – the error in analysis are based on measurements taken, compared to prepared standards with averages for Au, Pd and Pt calculated to be 4, 3 and 1 % respectively. The analytical error, associated with each loading and corresponding elution analysis, is given with the individual sample analysis results in Appendix B. From a sensitivity analysis it shows that an analytical underestimation of 1% for each sample also results in a 1% difference in the calculated recovery at 4 BVs.

2. Differences in carbon loadings from one elution experiment to another – Davidson and Duncanson (1977) found that the higher the gold loading on the activated carbon, the more efficient the elution process becomes, while Boshoff (1994) found the elution efficiency independent of the gold loading. Van Deventer and Liebenberg (2003) found that the elution of gold becomes more difficult with an increase in loading. The effect of Pt and Pd carbon loading on the elution recovery still has to be established and quantified and will be addressed in the thesis.
3. Influence of cations like Na^{+}, that force the elution recovery, curves to the right if adsorbed in higher quantities. – the shift in recovery due to the presence of Na^{+} still has to be established in the thesis.
4. Analysis inaccuracy due to 10x and 15x water dilutions - Sample dilutions for ICP analysis were done manually with a fixed 1 ml and an adjustable micro pipette. The adjustable micro pipette was calibrated by setting the pipette according to the required weight of sample required. This method of dilution is deemed to be fairly accurate, but the actual error may vary and is considered to be unknown. From a sensitivity analysis, it was found that a 1% error in the dilution (0.1 ml error 10 ml) will amount to a 1% error in the analysed result.

For a broader overview of the repeatability of the elution, the complete recovery curves corresponding to the statistical analysis in Table 3.14 are shown in Figure 3.14 to Figure 3.16. The recovery curves for Pd (Figure 3.14) and Pt (Figure 3.15) follow a very similar trend and fall into a distinctive band, which is characterized by the statistics given in Table 3.14. The curves lend confidence to the experiments showing that experiments can be repeated with the results being more or less 1.6 pp (Pd) and 1.8 pp (Pt) from the mean.

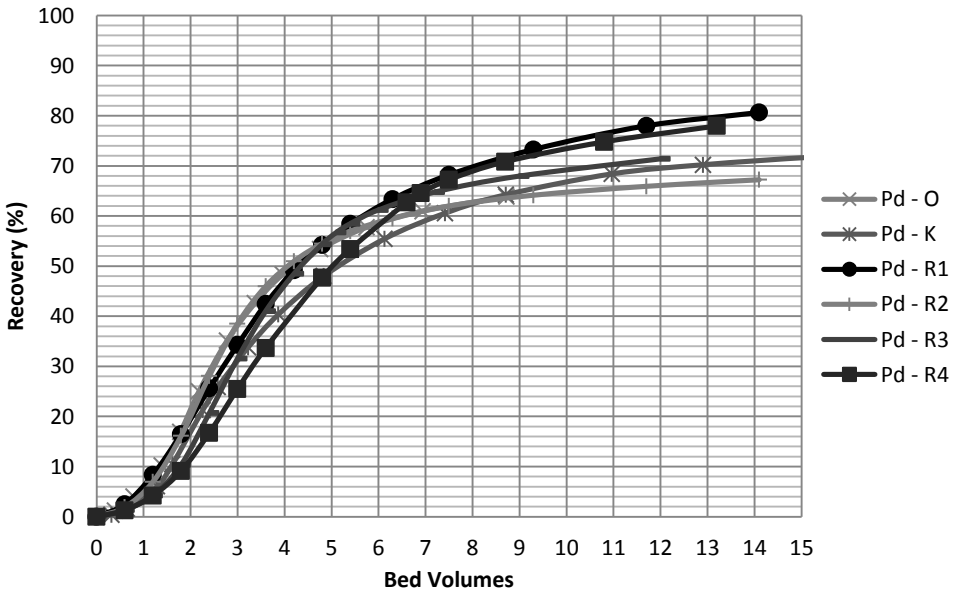


Figure 3.14: Repeatability recovery curves for the elution of Pd from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (0% NaCN, 0.6% NaOH) at an elution temperature of 80°C (Statistical analysis given in Table 3.14).

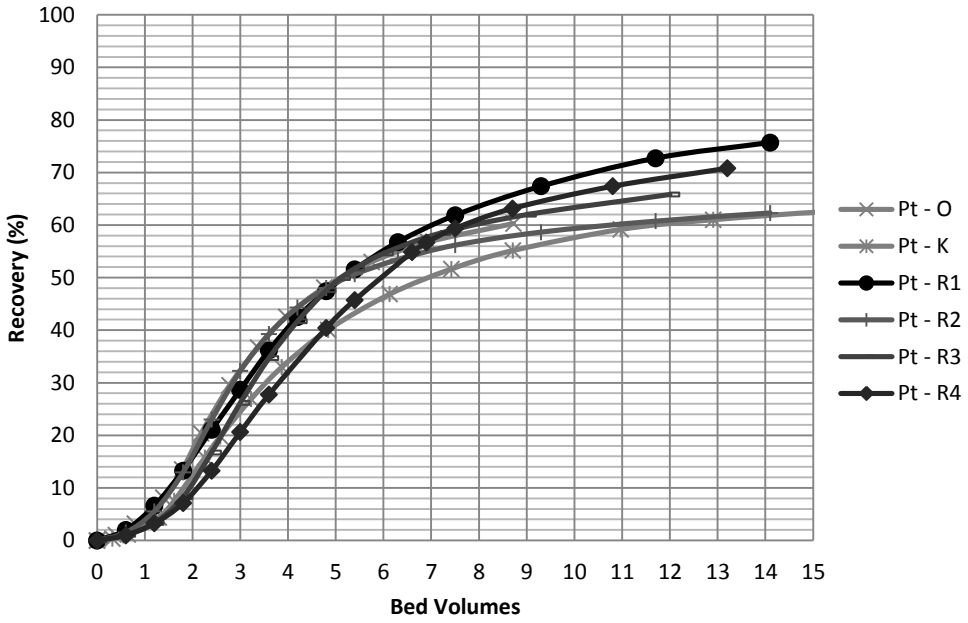


Figure 3.15: Repeatability recovery curves for the elution of Pt from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (0% NaCN, 0.6% NaOH) at an elution temperature of 80°C (Statistical analysis given in Table 3.14).

Where a rather distinctive trend exists for the Pt and Pd recovery curves, the recovery curve for Au is different. The elution kinetics for experiment R1 is considerably faster (0.48%/ BV) than the elution kinetics of experiment K (0.15 %/ BV) with the kinetics for each experiment remaining fairly constant over the period evaluated, which causes the graphs to open up and to become further apart with each BV. The difference, when experiment R1 is compared to experiment K, is great, but when compared to Pt and Pd, the Au recovery, however, remains very low (< 7 %) when Pt and Pd start to reach maximum elution values (around 15 BVs for Figure 3.14 and Figure 3.15). Due to the low recoveries for Au in general, the variance and standard deviation for Au are still fairly small at 0.9 when evaluated at 9 BVs (Table 3.14).

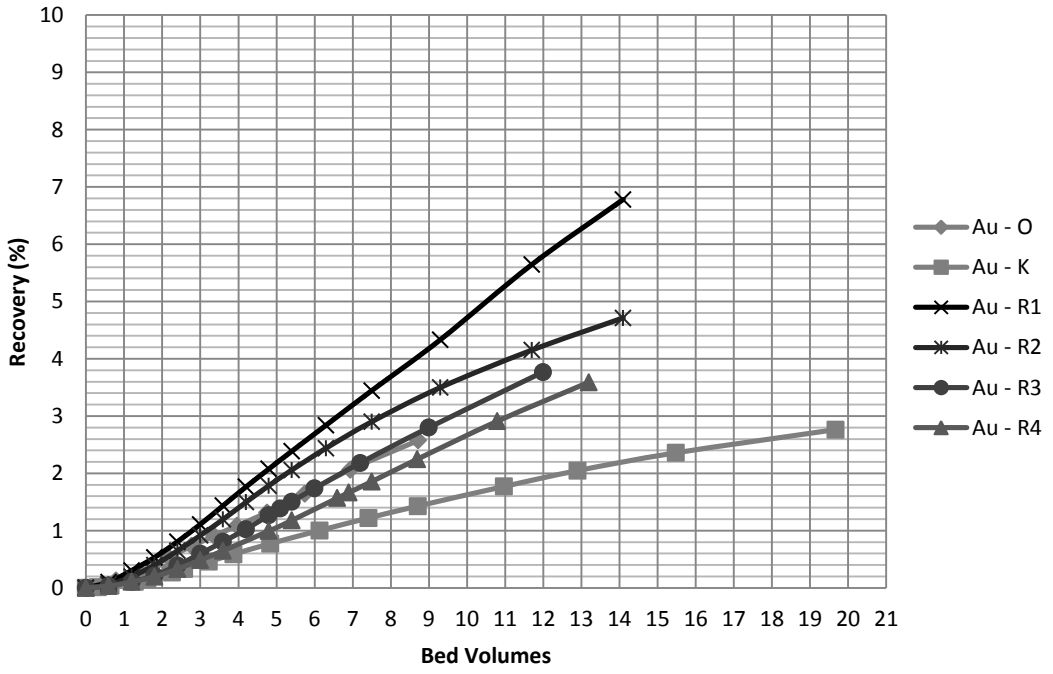


Figure 3.16: Repeatability recovery curves for the elution of Au from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (0% NaCN, 0.6% NaOH) at an elution temperature of 80°C. (Table 3.14)

Elution experiments with 1% NaCN and 0.6% NaOH pre-treament concentrations at 80°C were repeated and are shown in Table 3.15 and Figure 3.17. For experiment L, the sample that was taken at 4 BVs was contaminated with water, which ultimately resulted in one less data point, but was unfortunately exactly at 4 BVs where the curves were being evaluated. This led to the recovery curves in Figure 3.17 for experiment L having an almost straight line between 3 and 5 BVs instead of being curved upwards as per a typical S shaped curve. If a value is assumed at 4 BVs, which will fit the elution curve to replace the sample that was lost, the recovery can be recalculated and results in a 2% increase in recovery for both Pt and Pd at 4BVs and which ultimately reduces the standard deviation for Pd from 5.7 to 4.2 and the standard uncertainty from 4 to 3. The standard deviation for Pt is reduced from 9.2 to 7.8 and the standard uncertainty from 6.5 to 5.5. For consistency sake values, as sampled, were used and the elution profile and recovery curve were left unchanged.

Table 3.15: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈650 mg/kg of Pt, Pd and Au each) at 1% NaCN, 0.6% NaOH and at an elution temperature of 80°C.

	Pre-treatment		Recovery (%) 4 BV			Recovery (%) 5 BV			Recovery (%) 9 BV
Exp	NaOH (%)	NaCN (%)	Pd	Pt	Au	Pd	Pt	Au	Au
L	0.6	1	71	65	3.5	83	77	7	13
Q	0.6	1	79	78	3.4	86	87	4.8	13
Mean			75	71.5	3.45	84.5	82	5.9	13
Variance			32	84.5	0.005	4.5	50	2.42	0
Stdeviation			5.7	9.2	0.1	2.1	7.1	1.6	0.0

Standard uncertainty		4.0	6.5	0.05	1.5	5	1.1	0

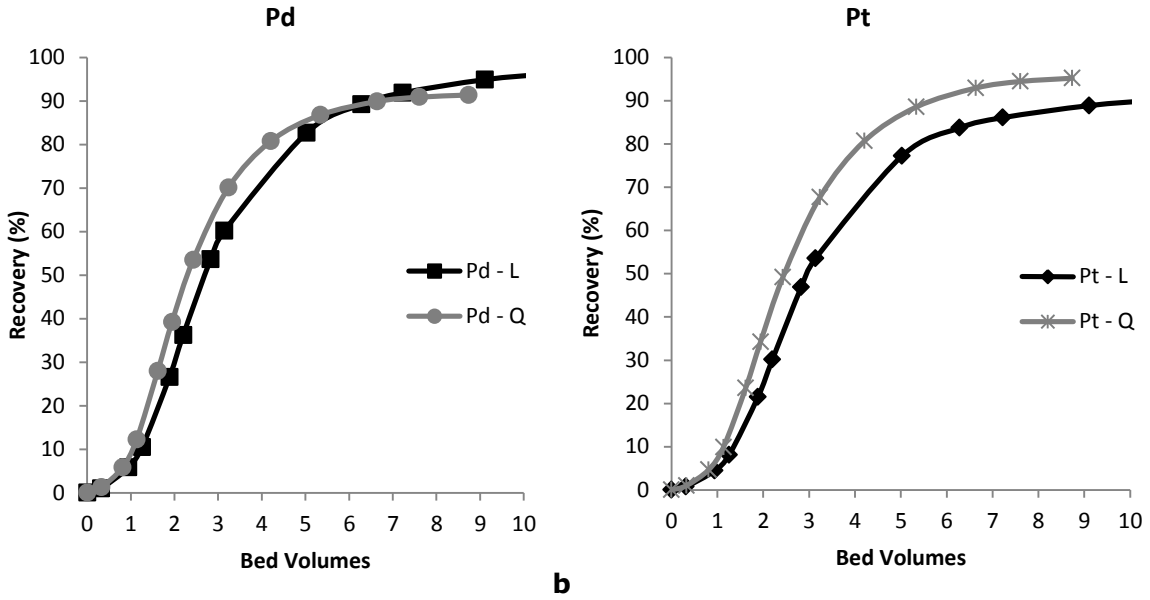
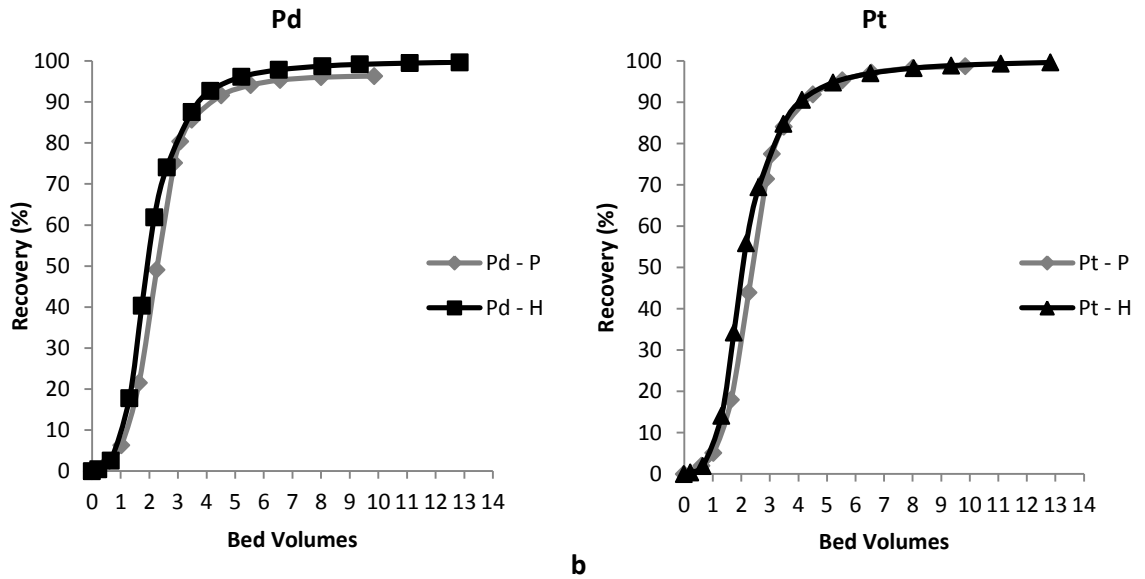


Figure 3.17: Repeatability recovery curves for the elution of a) Pd and b) Pt from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (1% NaCN, 0.55% NaOH) at an elution temperature of 80°C. (Table 3.15)

Elution experiments with 2% NaCN and 0.6% NaOH pre-treament concentrations at 80°C were repeated and are shown in Table 3.16 and Figure 3.18. The repeats yielded very similar results with 2% difference for both Pt and Pd at 4 BVs.

Table 3.16: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈650 mg/kg of Pt, Pd and Au each) at 2% NaCN and at an elution temperature of 80°C.

	Pre-treatment		Recovery (%) 4 BV			Recovery (%) 5 BV			Recovery (%) 9 BV
Exp	**NaOH (%)**	**NaCN (%)**	**Pd**	**Pt**	**Au**	**Pd**	**Pt**	**Au**	**Au**
P	0.6	2	94	92	6.5	97	96	10.5	31
H	0.6	2	92	90	7	96	94	12	31
Mean			93	91	6.75	96.5	95	11.25	31
Variance			2	2	0.125	0.5	2	1.125	0
Stdeviation			1.4	1.4	0.4	0.7	1.4	1.1	0.0
Standard uncertainty			1	1	0.25	0.5	1	0.75	0



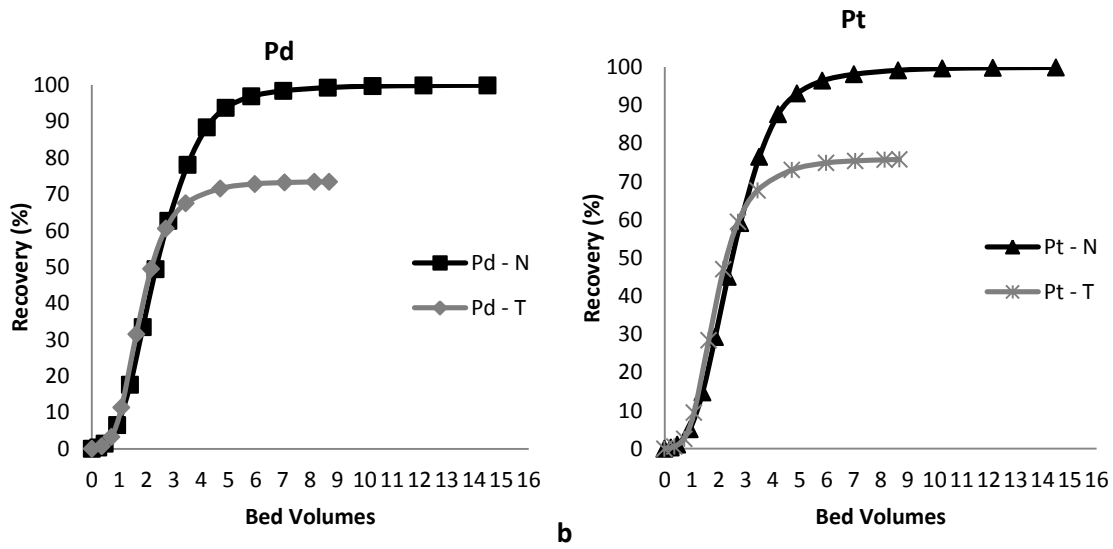
a b

Figure 3.18: Repeatability recovery curves for the elution of a) Pd and b) Pt from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.55% NaOH) at an elution temperature of 80°C. (Table 3.16)

Elution experiments with 4% NaCN and 0.6% NaOH pre-treament concentrations at 80°C were repeated and are shown in Table 3.17 and Figure 3.19. From Figure 3.19, it is seen that that the initial rate of elution for the two experiments is almost identical, but with a very clear difference between the plateau regions of the recovery curves. The difference here is related back to the assumption of an even distribution of the PGMs on the carbon after loading. If the amount of PGMs on the specific 12 g sample used for elution were estimated incorrectly, the recovery curve would be impacted with less (as in the case of experiment T) or more PGMs eluting than anticipated. To alleviate this problem, the carbon was mixed after adsorption and split into the different amounts of samples required, but it seems as if some error may still have occurred as in the case shown in Figure 3.19. As an example, over estimation of the carbon loading of experiment T by 50 mg/kg (7.6%) results in a 14% difference in recovery at 4BV, and the standard deviation is reduced from 10.6 to 4.2 and the standard error from 7.5 to 3 respectively.

Table 3.17: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈650 mg/kg of Pt, Pd and Au each) at 4% NaCN and at an elution temperature of 80°C.

Exp	Pre-treatment NaOH (%)	Pre-treatment NaCN (%)	Recovery (%) 4 BV Pd	Recovery (%) 4 BV Pt	Recovery (%) 4 BV Au	Recovery (%) 5 BV Pd	Recovery (%) 5 BV Pt	Recovery (%) 5 BV Au	Recovery (%) 9 BV Au
N	0.55	4	85	85	6.5	94	94	11	37
T	0.55	4	70	70	6.6	72	74	10	28
Mean			77.5	77.5	6.55	83	84	10.5	32.5
Variance			112.5	112.5	0.005	242	200	0.5	40.5
Stdeviation			10.6	10.6	0.1	15.6	14.1	0.7	6.4
Standard uncertainty			7.5	7.5	0.05	11	10	0.5	4.5



a b

Figure 3.19: Repeatability recovery curves for the elution of a) Pd and b) Pt from activated carbon (≈650 mg/kg of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (4% NaCN, 0.55% NaOH) at an elution temperature of 80°C. (Table 3.17)

High temperature elution repeatability (Steel column)

Repeat experiments for the elutions performed in the stainless steel columns were also performed and were found to be good at 130°C (Figure 3.20 and Table 3.18) and almost identical at 120°C (Figure 3.21 and Table 3.19).

Table 3.18: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈300 mg/kg of Pt, 230 mg/kg Pd and 500 mg/kg Au) at 2% NaCN and at an elution temperature of 130°C.

	Pre-treatment		Recovery (%) 4 BV			Recovery (%) 5 BV			Recovery (%) 9 BV
Exp	NaOH (%)	NaCN (%)	Pd	Pt	Au	Pd	Pt	Au	Au
T5	0.55	2	67	70	39	73	76	47	67
T6	0.55	2	71	76	43	77	82	51	69

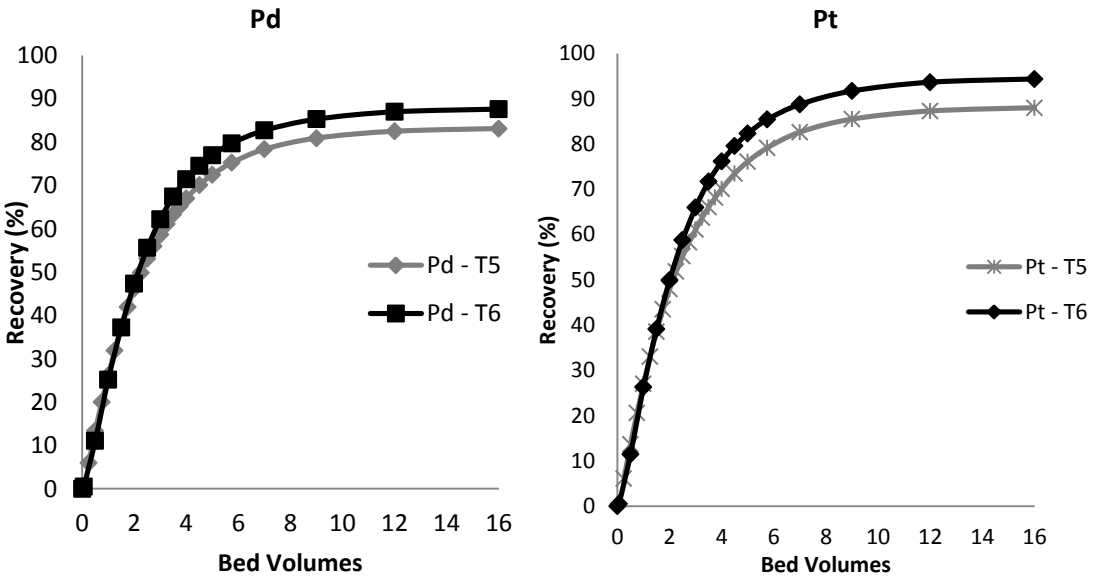


Figure 3.20: Repeatability recovery curves for the elution of a) Pd and b) Pt from activated carbon (≈300 mg/kg of Pt, 230 mg/kg Pd and 500 mg/kg Au) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.55% NaOH) at an elution temperature of 130°C. (Table 3.18)

Table 3.19: Repeatability test for the elution of Pd, Pt and Au from activated carbon (≈300 mg/kg of Pt, 230 mg/kg Pd and 500 mg/kg Au) at 2% NaCN and at an elution temperature of 120°C and a pre-treatment temperature of 80°C.

	Pre-treatment		Recovery (%) 4 BV			Recovery (%) 5 BV			Recovery (%) 9 BV
Exp	NaOH (%)	NaCN (%)	Pd	Pt	Au	Pd	Pt	Au	Au
T9	0.55	2	68	69	34	74	76	42	62
T10	0.55	2	68	68	37	74	75	45	64

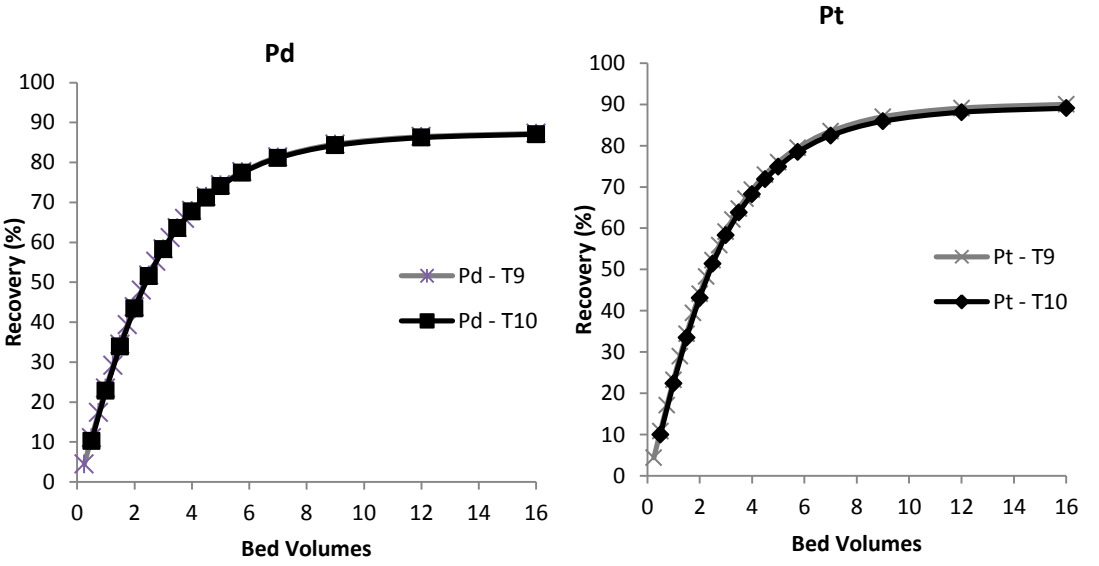


Figure 3.21: Repeatability recovery curves for the elution of a) Pd and b) Pt from activated carbon (≈300 mg/kg of Pt, 230 mg/kg Pd and 500 mg/kg Au) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.55% NaOH) at an elution temperature of 130°C. (Table 3.19)

Chapter 4

Results and discussion

4.1 Adsorption

The adsorption section can be considered as the heart of the CIS process and several adsorption experiments were therefore completed and discussed below.

4.1.1 Carbon and adsorption characterization

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used to study a sample's surface topography and composition by creating a high resolution image of the surface of the sample. Pleysier et al. (2008) reported that Au adsorbs predominantly onto the surface of the activated carbon and SEM was therefore used to investigate PGM adsorption on the surface and if any preferential areas of adsorption can be established.

Unloaded activated carbon was analysed first for surface characterisation and can be seen in Figure 4.22.

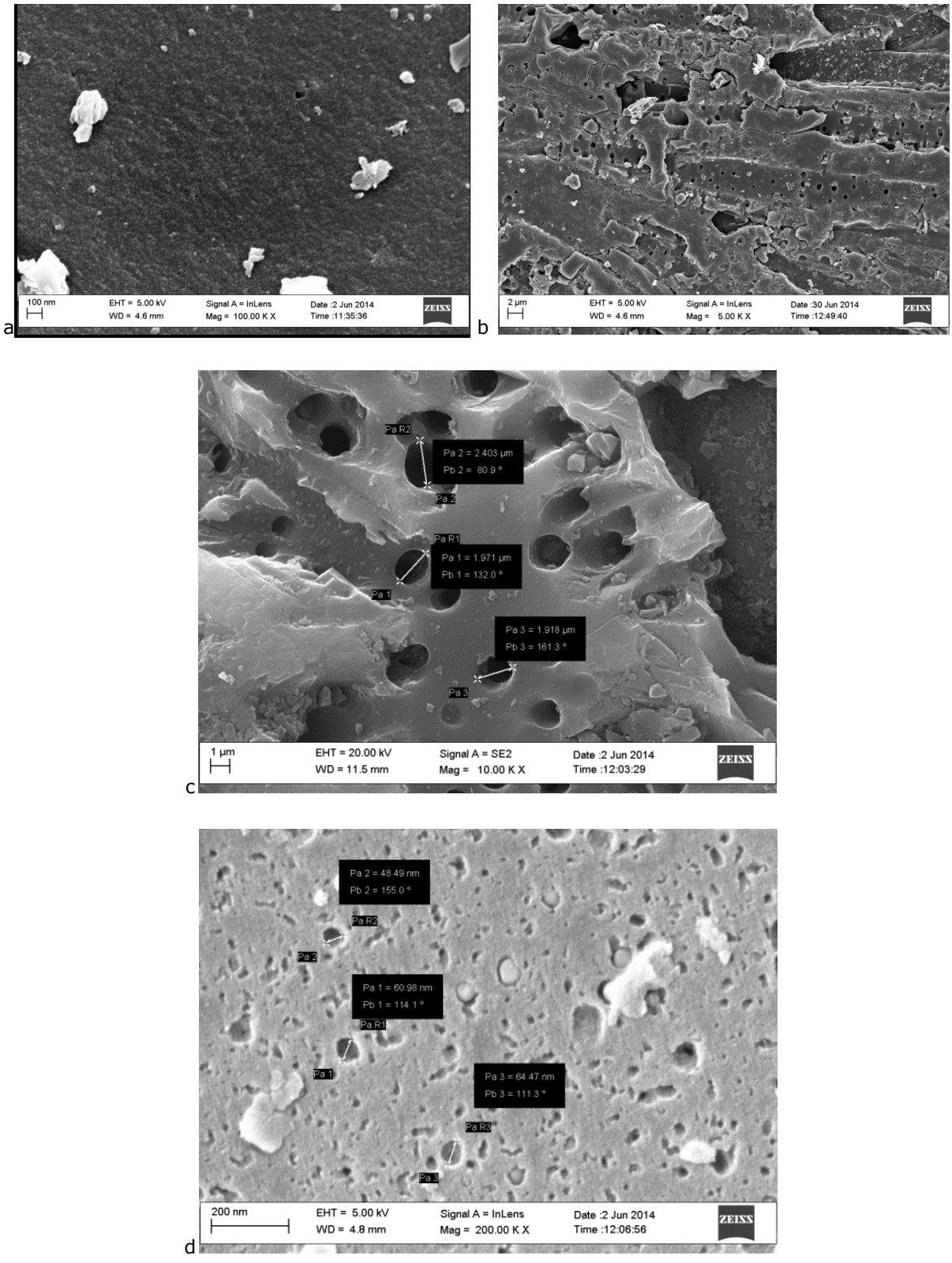


Figure 4.22: SEM images of the surface of blank activated carbon illustrating the porous surface carbon.

The SEM images (Figure 4.22) show the large surface area of the activated carbon with a great number of pores, of which some measured to be approximately 2 µm while other fell into the nanometre range (48 to 65 nm). The pores sizes as per Figure 4.22 are primarily for reference in relation to the image depicted and a great variability in number and size is expected over the entire carbon surface. Granules appearing brighter on the activated carbon are also seen and

create the impression of an impurity or a substance other than carbon, but were defined as pure carbon by SEM-EDS analysis.

Some of the carbon granules were sliced in half to reveal a cross section of the carbon (Figure 4.23). Large pores, made up of a number of smaller tubes, are visible, which create the impression of channels into the centre of the activated carbon.

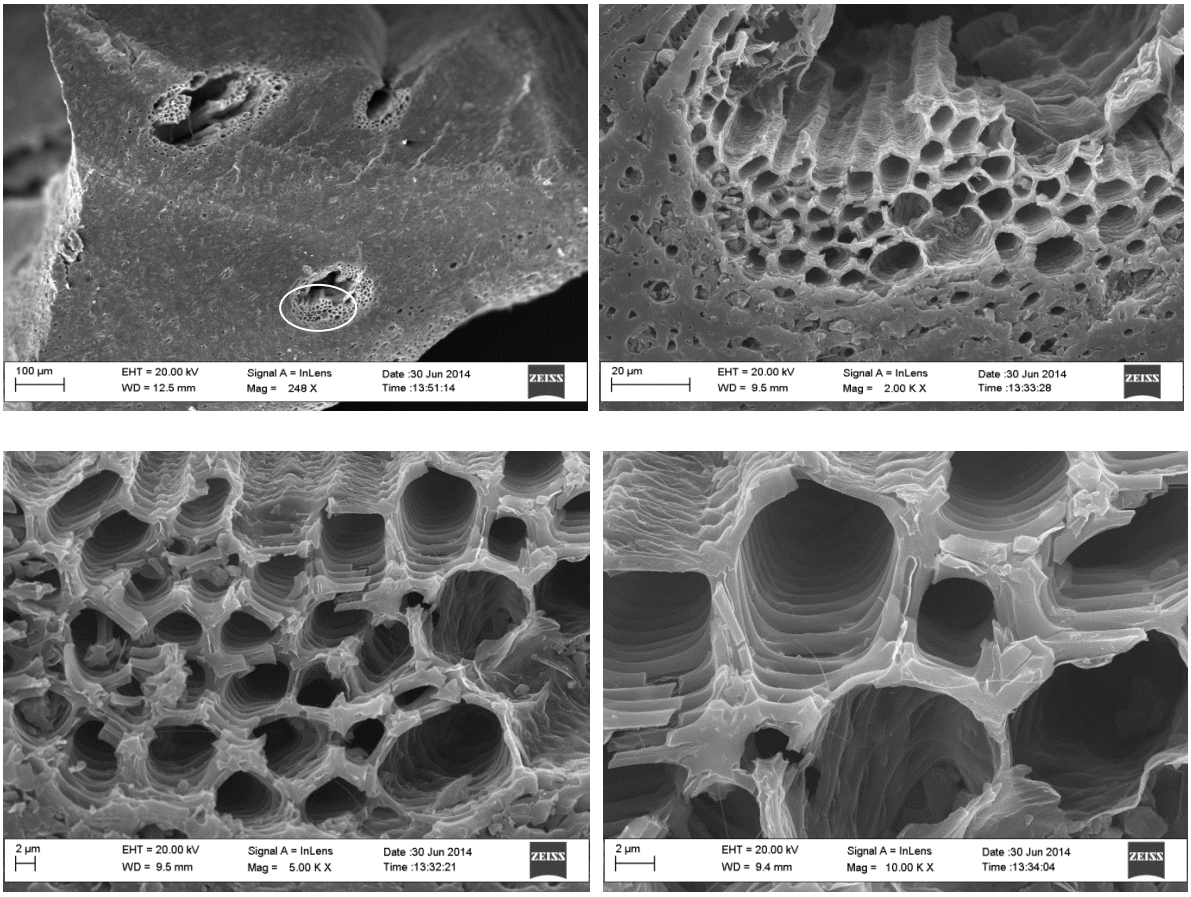


Figure 4.23: SEM images of a cross section of activated carbon revealing large pores to the inside of the activated carbon made up of several smaller diameter tubes (the same area of activated carbon is shown but with a higher degree of magnification in each consecutive image).

From a visual perspective, very little information could be obtained from images of loaded activated carbon. SEM-EDX spot analysis, however, did reveal the presence of metal on the surface as well as in the pores on the surface. Several measurements were taken to establish if preferential areas of adsorption exist. The positions of the spot analysis are detailed in Figure 4.24, while the amount of Pt measured for each spot is shown in Table 4.20.

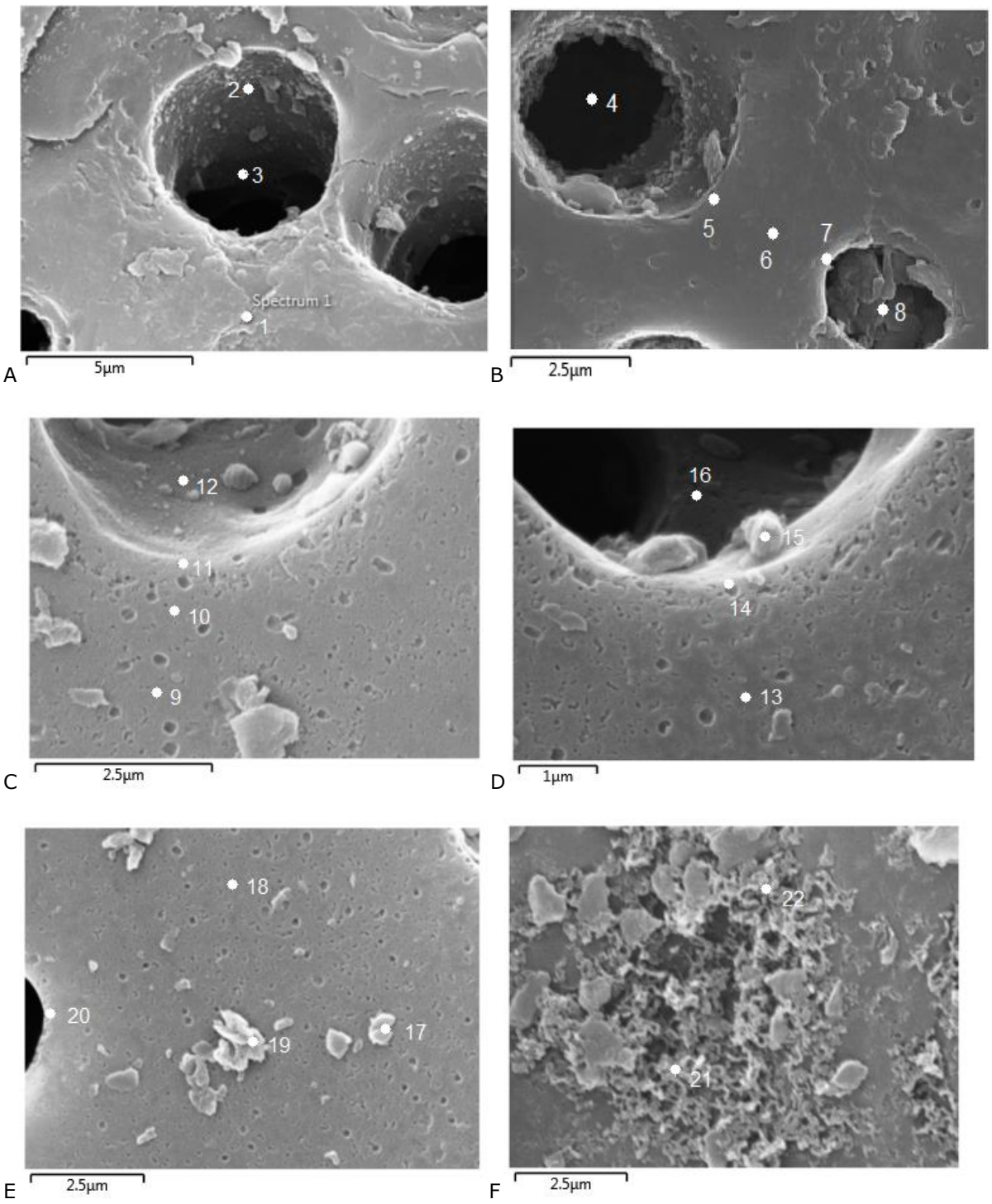


Figure 4.24: SEM-EDX spot analysis from Pt loaded activated carbon (Pt = 16800 mg/kg with no Pd and Au). Analysis of each point as per Table 4.20.[*]

[*] Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2014. The effect of temperature, cyanide and base metals on the adsorption of Pt, Pd and Au onto activated carbon, Hydrometallurgy, Vol 149, pp 132–142

Table 4.20: SEM-EDX spot analysis from Pt loaded activated carbon (Pt = 16800 mg/kg with no Pd and Au). Analysis of each point as per Figure 4.24.*

Image A	**1**	**2**	**3**		
Pt (wt %)	1.4	3.2	5.1		
Image B	**4**	**5**	**6**	**7**	**8**
Pt (wt %)	18.3	2.4	2	5	3.8
Image C	**9**	**10**	**11**	**12**	
Pt (wt %)	2.6	2.9	2.7	3.8	
Image D	**13**	**14**	**15**	**16**	
Pt (wt %)	1.6	2.0	2.3	2.7	
Image E	**17**	**18**	**19**	**20**	
Pt (wt %)	1.8	1.7	1.6	3.9	
Image F	**21**	**22**			
Pt (wt %)	2.3	2.7			

From the spot analyses, measurements of Pt on the surface mostly range between 1.4 and 5 % with one measurement as high as 18 % for a total loading of 16800 mg/kg. Furthermore, it seems as if the Pt adsorption becomes more concentrated as it gets closer to the pores with the highest concentration of Pt measured in the pores. The higher concentrations of Pt in the pores can be seen in images A to C as per Figure 4.24. Image F shows no pores, but a very rough carbon surface with Pt measurements of 2.7 and 2.3 %.

Similar spot analyses were done for carbon loaded with Pt, Pd and Au and the results can be seen in Figure 4.25 and Table 4.21. Au surface measurements ranged between 0.8 and 3.9 % for a Au loading of 16590 mg/kg. The higher gold concentrations were again found to be in the pores. At lower Pt and Pd loadings of respectively 2140 and 1430 mg/kg, the concentration on the surface was more evenly distributed with a higher concentration in the pores less evident.

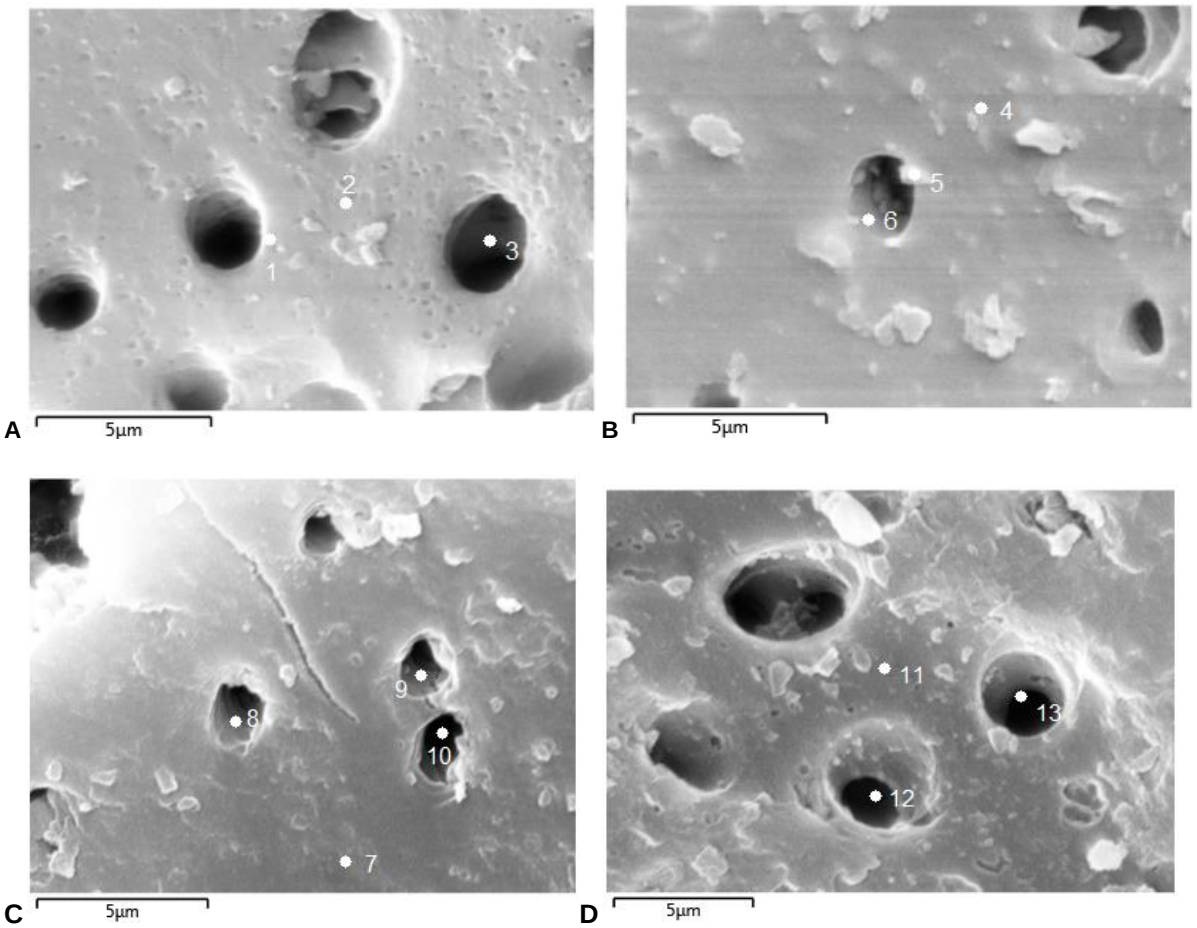


Figure 4.25: SEM-EDX spot analysis from PGM loaded activated carbon (Pt = 2140 mg/kg, Pd = 1430 mg/kg and Au = 16590 mg/kg). Analysis of each point as per Table 4.21.*

Table 4.21: SEM-EDX spot analysis from PGM loaded activated carbon (Pt = 2140 mg/kg, Pd = 1430 mg/kg and Au = 16590 mg/kg). Analysis of each point as per Figure 4.25.

Image A	**1**	**2**	**3**	
Pt (wt %)	0.6	0.6	0.6	
Pd (wt %)	0.6	0.3	0.9	
Au (wt %)	2.4	1.8	3.9	
Image B	**4**	**5**	**6**	
Pt (wt %)	0.4	0.5	0.5	
Pd (wt %)	0.4	0.5	0.5	
Au (wt %)	2.2	2.2	2.9	
Image C	**7**	**8**	**9**	**10**
Pt (wt %)	0.2	0.3	0.2	0.3
Pd (wt %)	0.3	0.2	0.3	0.3
Au (wt %)	1.3	1.2	1.4	1.6
Image D	**11**	**12**	**13**	
Pt (wt %)	0.2	0.5	0.9	
Pd (wt %)	0.3	0.5	0.5	
Au (wt %)	0.8	1.4	2.0	

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2014. The effect of temperature, cyanide and base metals on the adsorption of Pt, Pd and Au onto activated carbon, Hydrometallurgy, Vol 149, pp 132–142

For a study of the adsorbed cyanide complexes greater magnification is required, which can be achieved through transmission electron microscopy (TEM). An image of blank activated carbon of approximately 40 x 40 nm (compared to 15 x 15 µm images with the SEM) to establish the atomic structure and character can be seen in Figure 4.26. From Figure 4.26 the graphene layers of the activated carbon are visible and closely resemble the random relative orientations of layers associated with disordered carbons (Aso et al. 2004, Marsh and Rodríguez-Reinoso, 2006) as identified by skeletonised images derived from TEM. Well-ordered carbon, as qualitatively described by Aso et al. (2014), corresponds to carbon with a more planar structure and with some stacking along one direction, while disordered carbon is less crystalline and observed as highly curved fringes with almost no stacking. The disordered activated carbon related to a higher reactivity, which Aso et al. (2004) ascribed to the higher concentration of defects in the carbon. The interlayer spacing between lattice fringes as per the circled area in Figure 4.26 was measured to be of 2.5 Å. The bright stripes, as in the circled area of Figure 4.26, are called lattice fringes and they can appear in one or more directions. If the specimen is very thin, these fringes can be interpreted as the projection of tunnels between columns of atoms, while the dark lines are the atoms themselves (Rose, 2006).

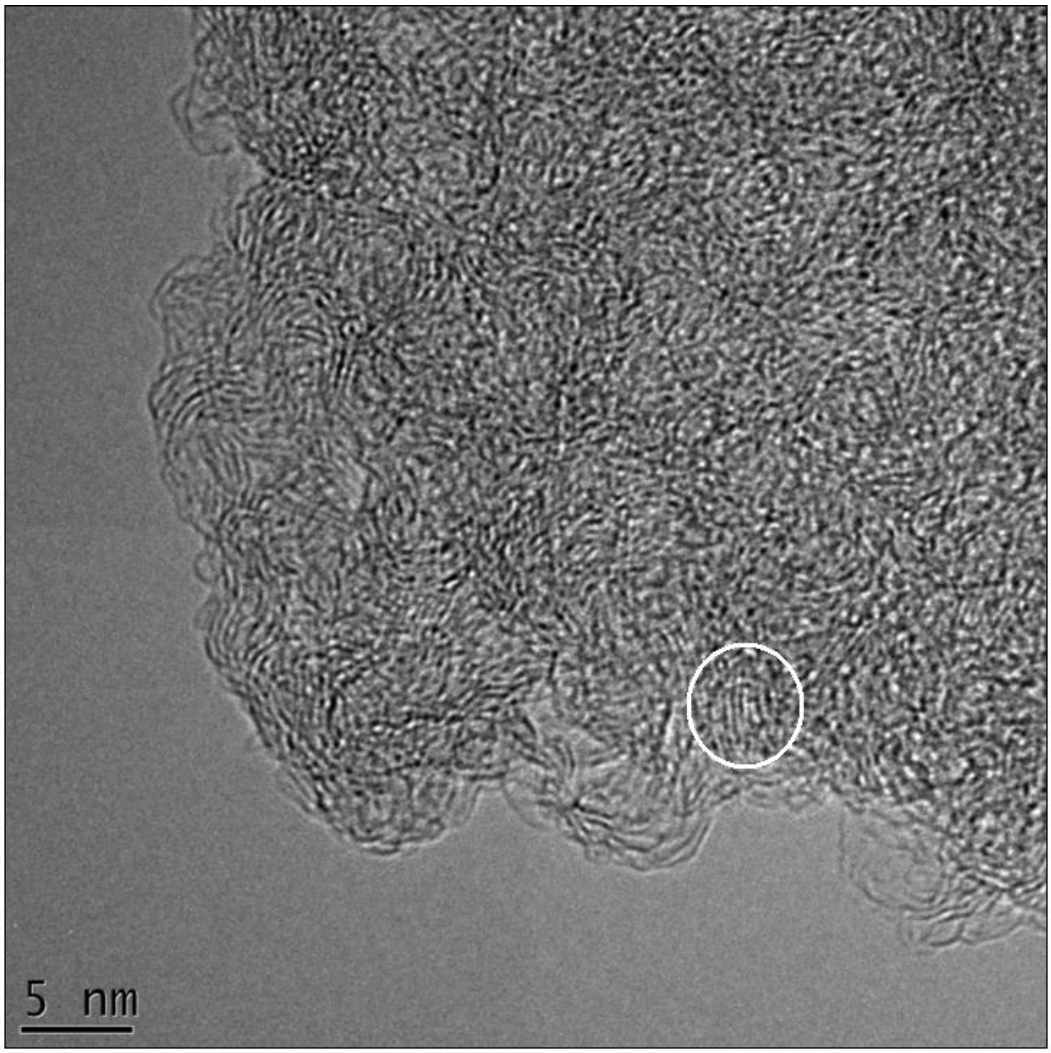


Figure 4.26: TEM image of unloaded activated carbon with an interlayer spacing between lattice fringes of 2.5 Å as per the circled area.

TEM images of activated carbon loaded with aurocyanide complexes showed a very similar image to that of the unloaded activated carbon. For this particular sample, TEM-EDX indicates a 1.8 % gold analysis (Table 4.22 and

Figure 4.28) and there does seem to be an increase in linear fringe stacks. Lattice fringes measurements of the circled area in Figure 4.27 indicate a spacing of 3.5Å (Figure A.105 in Appendix A) and when compared to the primary interplanar spacings expected in lattice images of metallic Au particles, which are typically 2.35 and 2.04 A°, corresponding to the (111) and (200) (*hkl*) reflections respectively (Allard et al. 2009), it can be concluded that the structure circled in Figure 4.27 is not metallic gold. TEM images by Aso et al. (2004) resembling the carbon in this study revealed almost no lattice fringe measurements for the activated carbons studied greater than 3Å and the structures found in Figure 4.27 may very well indicate linear stacks of $Au(CN)_2^-$.

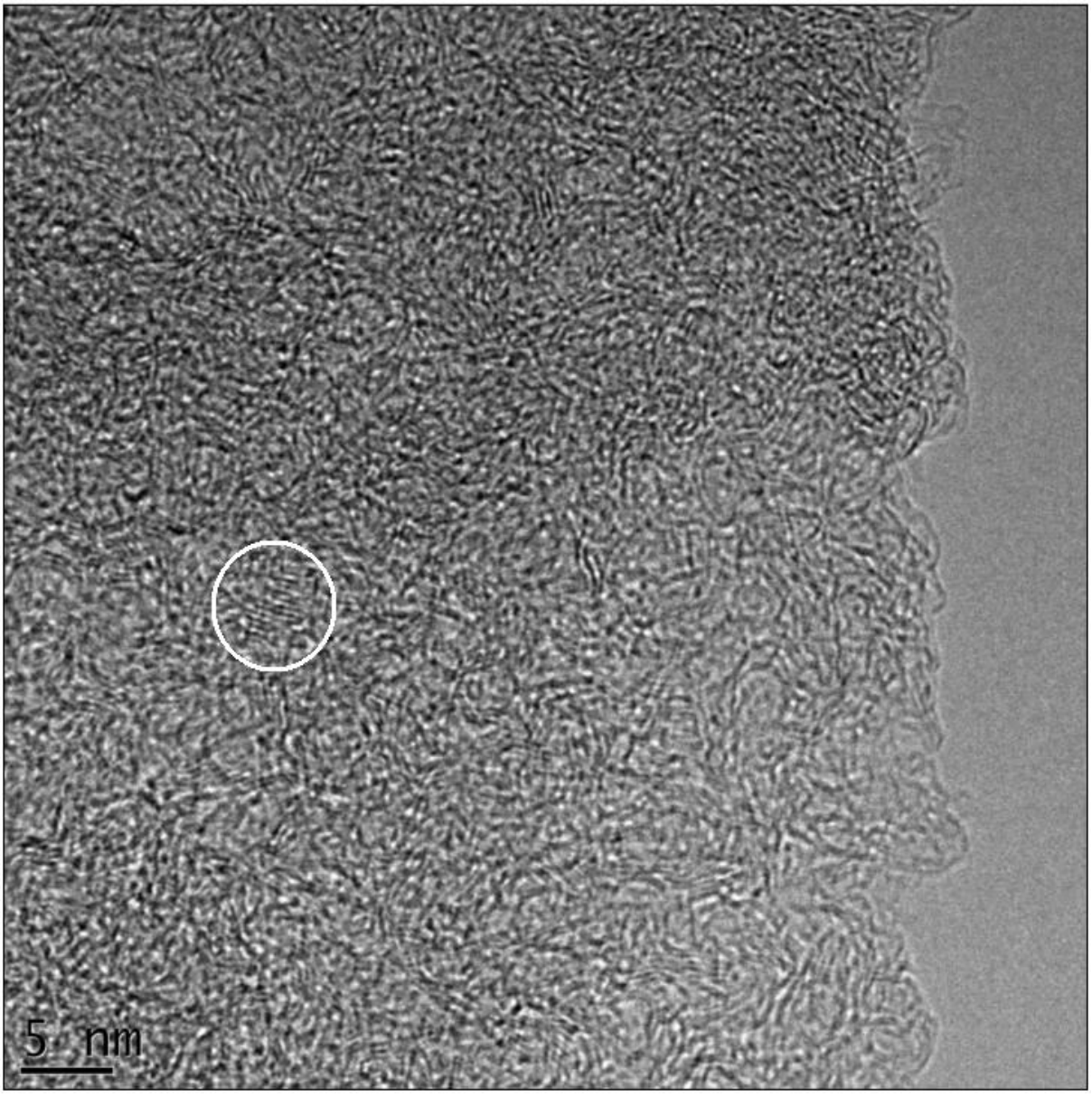


Figure 4.27: TEM image of loaded activated carbon loaded with aurocyanide complexes (Au - 16000 mg/kg)

Table 4.22: TEM-EDX sample composition for activated carbon loaded with aurocyanide complexes

Element	Weight (%)
C	94.6
O	3.2
Mg	0.1
Ca	0.4
Au	1.8

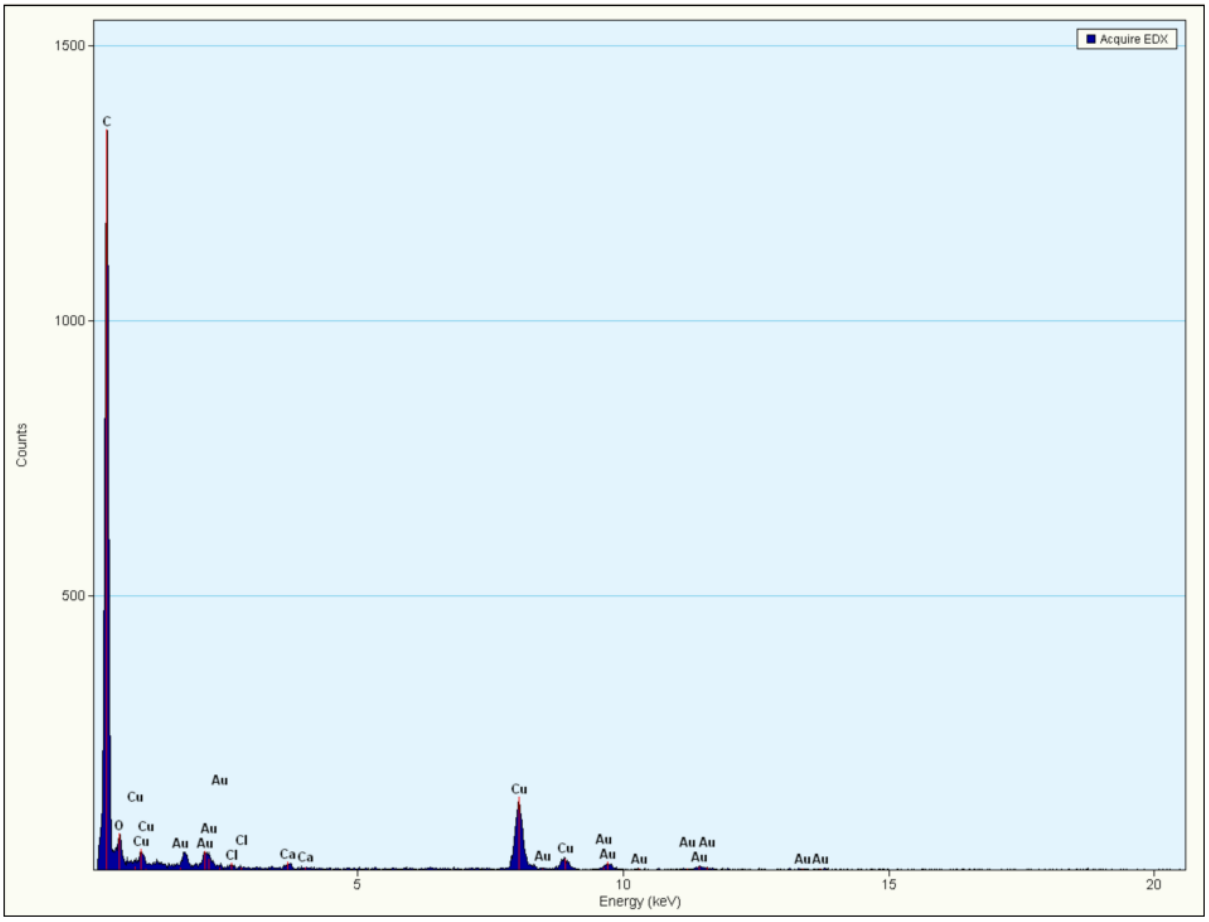


Figure 4.28: EDX spectrum over the entire region as shown by Figure 4.27 for activated carbon loaded with aurocyanide complexes placed on a copper grid.

TEM images of activated carbon loaded with Pt cyanide complexes can be seen in Figure 4.29. From Figure 4.29, a structure (≈ 15 nm in length) quite different to that of the activated carbon as established by Figure 4.26, can be seen and resembles the Pt metal nanocrystals on a carbon coated grid studied by Song et al. (2005) and the interplanar distance measured here of 2.22Å (Figure A.108 in Appendix A) compares relatively well with the inter planar distance of 2.26Å for the {111} planes of the Pt metal cuboctahedra studied by Song et al. (2005). TEM-EDX analysis of the area shown in Figure 4.29 indicated 0.6 % Pt. The image studied here and the resemblance to Pt metal on activated carbon studied from literature (Song et al, 2005) certainly points to the possibility of the platinum cyano complex being reduced on the activated carbon and therefore warrants a TEM focussed investigation into the subject. Mpinga et al. (2014) reported a reduction potential for $Pt(CN)_4^{2-}$ of 0.05 V while Adams (1991) gave a range of between -0.16 to +0.16 V for

commercial activated carbon. If these values are correct, it would certainly point to the possibility of reduction of the Pt complex occurring.

TEM images for activated carbon loaded with Pd cyanide complexes were also studied, but the images studied only resembled that of unloaded activated carbon with EDX measurements of 0.35 % Pd. These images can be seen in Figure A.109 to Figure A.110 in Appendix A. Mpinga et al. (2014) reported a reduction potential for $Pd(CN)_4^{2-}$ of -0.46 V and for Au, 0.62 V.

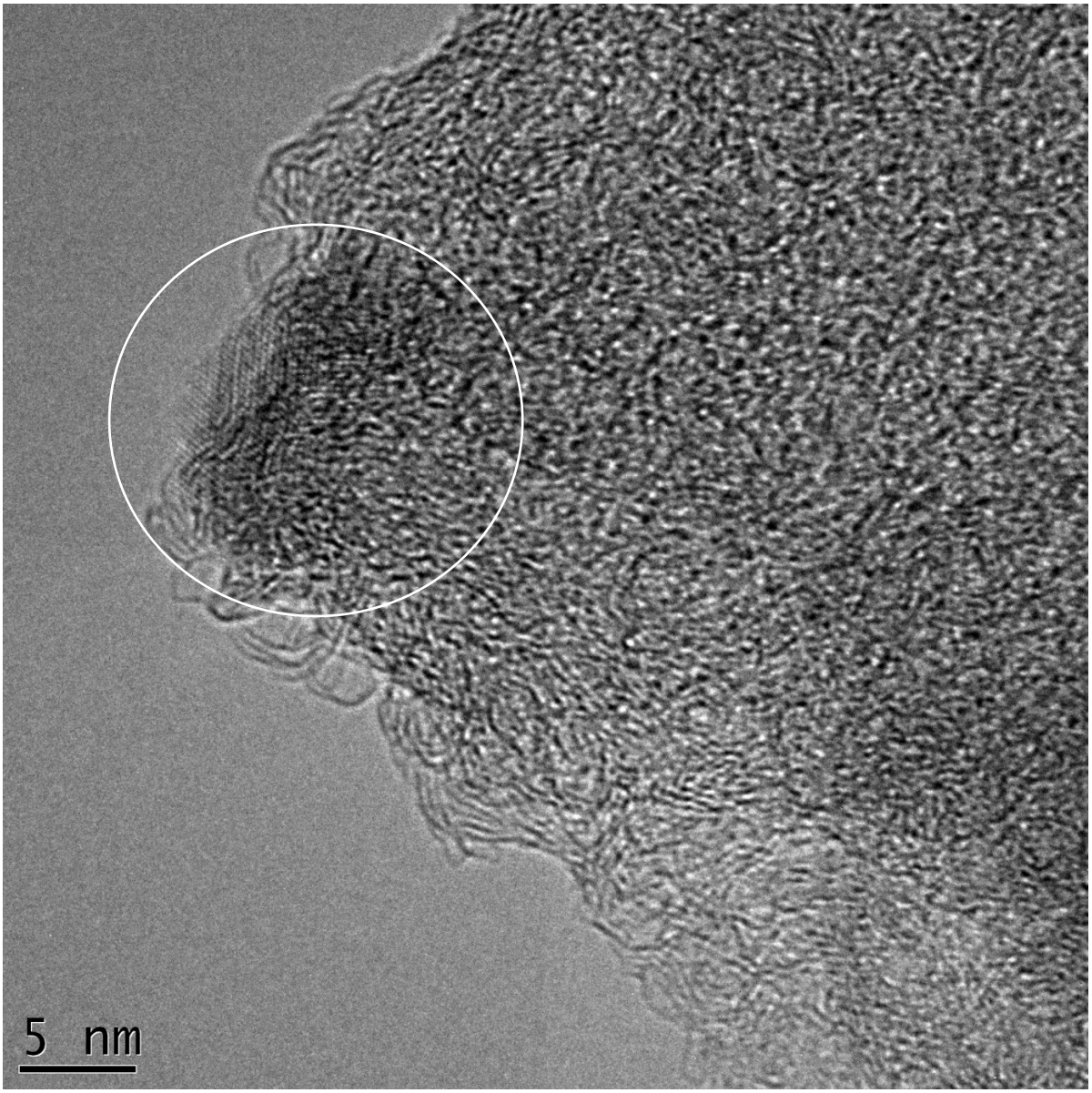


Figure 4.29: TEM image of loaded activated carbon loaded with platinum cyanide complexes (Pd - 16000 mg/kg)

Conclusion on carbon and adsorption characterization

PGM loaded as well as unloaded activated carbon has been studied with a scanning and transmission electron microscope (SEM and TEM). None of the PGM cyano complexes were visible through the SEM, but spot analysis of the surfaces indicated an adsorption preference closer and inside the pores. TEM did not conclusively reveal aurocyanide or clusters of aurocyanide

complexes, but analysis of a Pt loaded activated carbon did reveal a structure closely resembling an image of Pt metal on a carbon coated surface (Song et al. 2005). This may point to the reduction of the Pt cyano complex on the activated carbon, but further studies in this regard are recommended.

4.1.2 Equilibrium isotherms*

An equilibrium isotherm is a mathematical expression relating the concentration of the adsorbate in the liquid phase with the concentration of the adsorbate on the adsorbent at constant temperature. No isotherm data, or any data regarding the capacity of activated carbon for Pt and Pd, is available, except for Desmond et al. (1991), who investigated different PGM cyanide upgrading technologies and disregarded activated carbon based on the low PGM loadings of 70 troy ounces PGM/short t AC (2400 mg/kg AC) achieved. No additional information regarding the experiment is, however, available. Single component equilibrium isotherms for Pt and Pd at room temperature (25°C) in the absence of free cyanide and buffered to a pH of 9.5 with a loading time of 72 hours have therefore been developed.

The assumption that a loading time of 72 hours is adequate for the determination of the isotherm is based on the work of Liebenberg and Van der Merwe (1997), who deemed a pseudo equilibrium time of 72 hours as effective for the fundamental modelling of gold CIP/CIL circuits, although true gold adsorption equilibrium will take more than three weeks to reach. Since Pt and Pd cyanide complexes tend to adsorb at a slower rate than Au cyanide complexes (Mpinga, 2012), a kinetic rate adsorption experiment was conducted from a sufficiently high concentration (30 mg/L each) of Pt and Pd to determine when equilibrium for these two metals will be reached. The objective of this loading experiment was, however, twofold:

1. To validate the assumption of 72 hours for equilibrium for the development of the equilibrium isotherms.
2. To load a high amount of Pt and Pd onto the activated carbon to determine the influence of a higher loading of PGMs on the elution efficiency.

The kinetic rate of adsorption from the high concentration (30mg/L) Pt and Pd solution is shown in Figure 4.30.

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2014. The effect of temperature, cyanide and base metals on the adsorption of Pt, Pd and Au onto activated carbon, Hydrometallurgy, Vol 149, pp 132–142

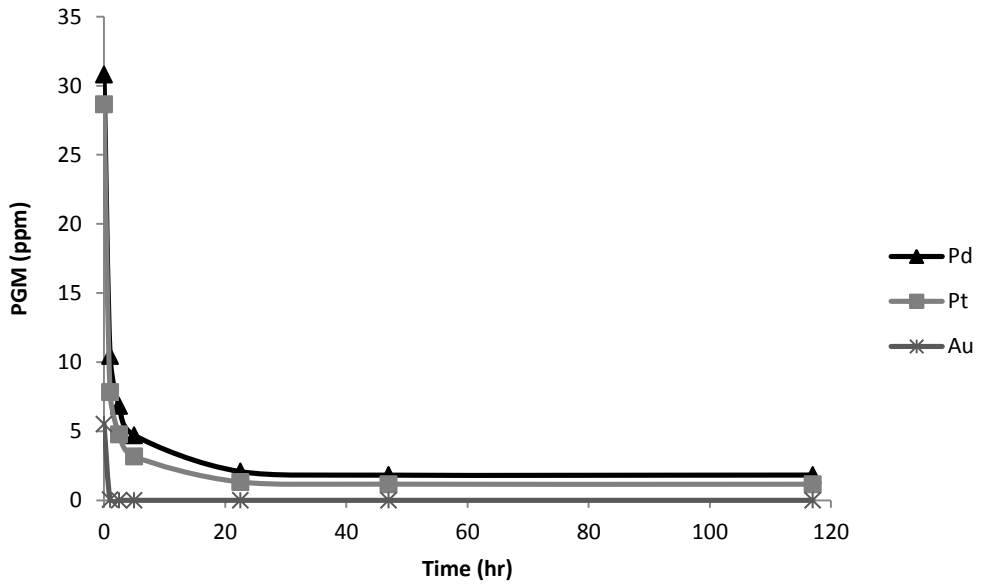


Figure 4.30: Activated carbon loading from a high concentration PGM (30.8 mg/L Pd, 28.7 mg/L Pt, 5.5 mg/L Au) solution. (CN = 0, pH = 9.5, Temperature = 25°C)

Initial adsorption of the PGMs occurs rapidly with 66% of the Pd, 73% of the Pt and 99% of the Au adsorbed within the first hour after which the rate of adsorption starts decreasing rapidly for Pd and Pt with steady state (pseudo-equilibrium) reached after 47 hours with 1.9 mg/L Pd and 1.2 mg/L Pt left over in solution. 100% adsorption of Au occurrs within the first 2.5 hours. From Figure 4.30 the loading of PGMs over time on the activated carbon can be calculated and is shown in Figure A.111 in appendix A. The maximum loading capacity achieved, is shown in Table 4.23.

Table 4.23: Equilibrium PGM loading on activated carbon achieved loaded from a high concentration PGM solution (30.8 mg/L Pd, 28.7 mg/L Pt, 5.5 mg/L Au). Equilibrium solution concentration = 1.9 mg/L Pd and 1.2 mg/L Pt.

Loading on AC (mg/kg)	
Au	688
Pd	3625
Pt	3436
Total PGMs	7748

The adsorption time of 72 hours to reach equilibrium was deemed an appropriate contact time to determine the Pt and Pd isotherms. The most widely used isotherm for the adsorption of gold onto activated carbon is the Freundlich (Eq. 4.1) and the Langmuir isotherm (Eq. 4.2) (Woollacott and Nino de Guzman, 1993). Table 4.24 shows the equilibrium constants for the Freundlich equation (Eq.4.1) fitted to the experimental data.

$$Q = A.C^n \tag{4.1}$$

$$Q = \frac{Q_m KC}{1+KC} \tag{4.2}$$

The constant A for the Freundlich isotherm (Eq. 4.1) is a function of the energy of adsorption and temperature and a measure of adsorption capacity, while n represents adsorption intensity or otherwise stated it is an indication of the effect of concentration on the adsorption capacity (Öser et al. 1999). For the Langmuir isotherm, Q_m is equal to the maximum adsorption of a specific metal (mg/l) and K reflects quantitatively the affinity between the adsorbent and adsorbate (Woollacott and Nino de Guzman, 1993, Öser et al. 1999). Both of these isotherm models were linearized and fitted to the equilibrium data with the Freundlich isotherm (Eq. 4.1) representing the data better than the Langmuir isotherm (Eq. 4.2) which did not fit (R^2 = 0.39). Table 4.24 shows the equilibrium constants for the Freundlich equation, while the linearization method and determination of the constants are shown in Appendix D.

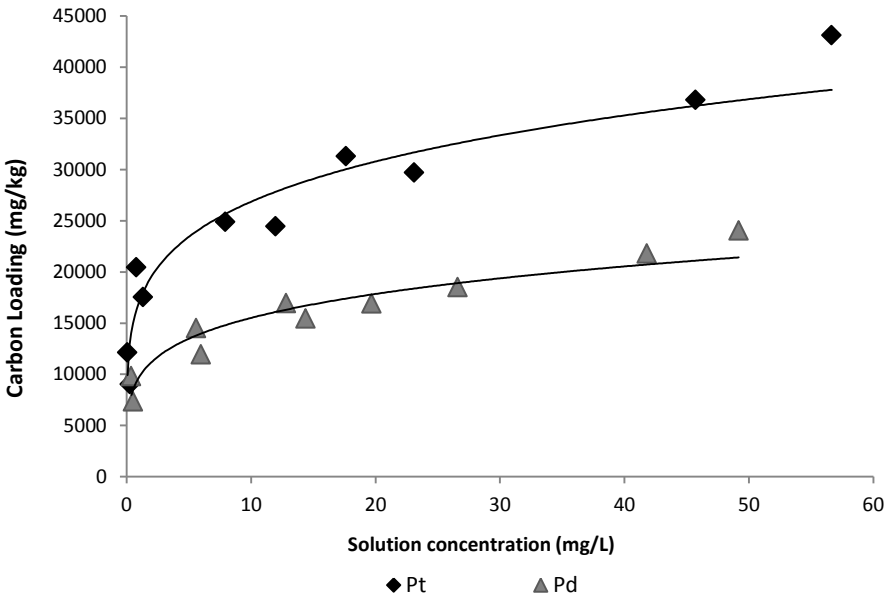


Figure 4.31: Single component equilibrium isotherms for Pt and Pd after 72 hours of adsorption (25°C, pH - 9.5, no free [CN], 1100 mg/L Na^+) with the Freundlich isotherm (Eq. 4.1) fitted to the data.

Table 4.24: Numerical constants for the single component Freundlich isotherms for Pt and Pd.

	A	n	R^2
Pt	17068	0.1969	0.87
Pd	9729	0.2026	0.90

To serve as a reference, the Pt and Pd isotherms were plotted with gold isotherms obtained from literature and are shown in Figure 4.32. Direct comparison to gold isotherms found in literature is, however, difficult at best due to the many factors that affect the adsorption of metal cyanide complexes such as the activity of the activated carbon used, the adsorption equipment and stream constituents like oxygen, electrolytes, pH and cyanide (Fleming and Nicol, 1984, Van der Merwe and Van Deventer, 1988, Woollacott and Nino de Guzman, 1993).

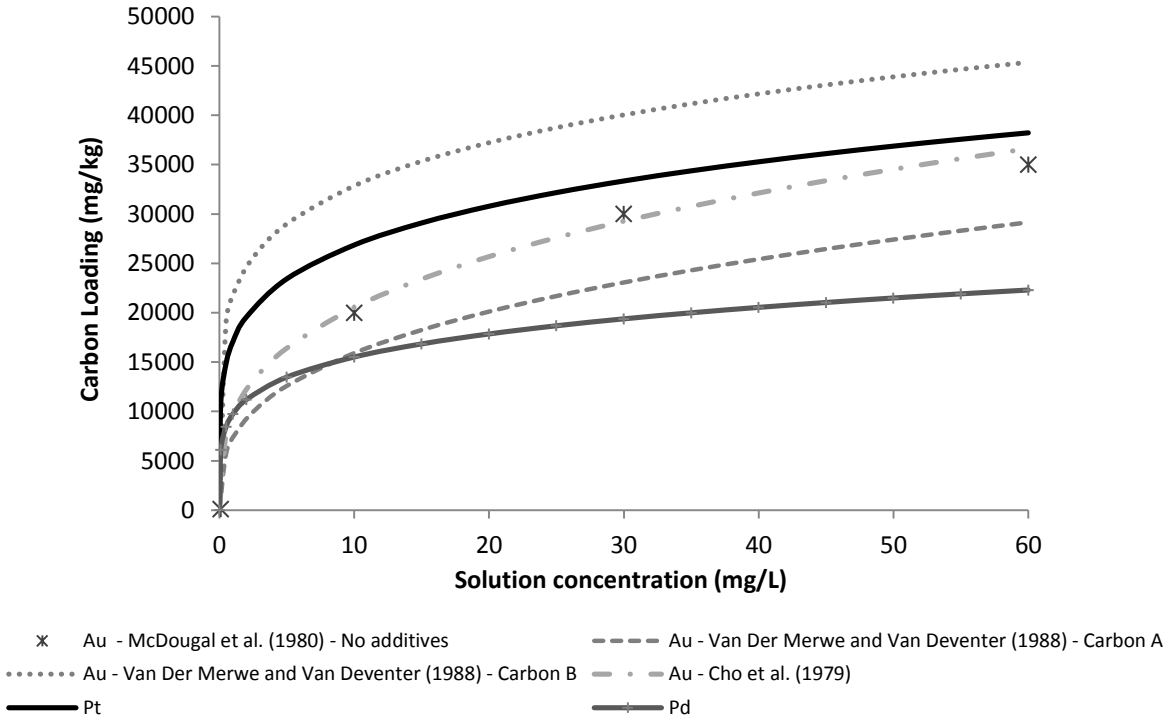


Figure 4.32: Single component equilibrium isotherms for Pt and Pd after 72 hours of adsorption (25°C, pH - 9.5, no free [CN], 1100 mg/L Na^+) compared gold adsorption isotherms from literature.

The gold isotherm (Figure 4.32) developed by McDougal et al. (1980) contained no additives and was completed at room temperature with a coconut based activated carbon with a BET of 1000 m^2/g. In addition, McDougal et al. (1980) also found that the gold adsorption almost doubled when 1840 mg/L Na^+ cations (0.08M $NaClO_4$) were added to the solution. For the gold isotherms developed by Van Der Merwe and Van Deventer (1988), experiments were completed at room temperature for two different coconut shell activated carbons at a pH of 8.5, which were adjusted with KOH and HCl. Isotherms showed by Cho et al. (1979) at 25°C and 25mg/L free cyanide (Freundlich isotherm parameters: A = 9759 and n = 0.323), fell in a similar range as the Au and Pt isotherms in Figure 4.32. From Figure 4.32 it is therefore concluded that the Pt isotherm developed here, although high in Na^+ cations, which drive adsorption (McDougal et al. 1980), falls into a comparable range to that of gold adsorption. The Pd isotherm is shown to be significantly lower than the Pt isotherm at the same conditions and lower than any of the gold isotherms discussed from literature.

Vorob'ev-Desyatovskii et al. (2012) suggested that a strong contribution to the difference in adsorption between metal cyanide complexes is attributed to the geometry of the complex. Linear complexes like $[Au(CN)_2]^-$, $[Ag(CN)_2]^-$, $[Cu(CN)_2]^-$ and $Hg(CN)_2$ adsorb strongly onto activated carbon, while planar complexes like $[Pt(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ to a lesser extent (Mpinga, 2012) followed by distorted planar complexes such as $[Cu(CN)_3]^{2-}$. Tetrahedral ($[Cu(CN)_4]^{3-}$, $[Ag(CN)_4]^{3-}$, $[Zn(CN)_4]^{2-}$, $[Cd(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$) and octahedral complexes ($[Rh(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Pt(CN)_6]^{2-}$) do not adsorb onto activated carbon. The adsorption mechanism that Vorob'ev-Desyatovskii et al. (2012) proposed, involved the cyanometallate ion with a linear structure or a square planar structure to directly bind to active

centres on the activated carbon surface and in the pores, which act like anchors through the formation of donor-acceptor bonds. Further cyanometallate anions are then added by building "stacks" of planar ions or "columns" with linear structures through the formation of metallophilic bonds. Such bonds are impossible with cyanometallate complex anions with tetrahedral or octahedral structures, and for these structures an ion exchange and a nonspecific physical adsorption are deemed a more probable mechanism. The greatest amount of the active centres is concentrated in micropores of activated carbons and near them on the adsorbent surface, which agrees with element analysis from SEM images of loaded activated carbon from this study (Figure 4.24 and Table 4.20), which shows a higher concentration of PGMs closer and inside the pores. As opposed to the above mentioned examples, Adams (1992) found that the affinity of carbon for $[Au(CN)_4]^-$, which has a planar structure (Shorrock et al. 2003), is greater than for the linear $[Au(CN)_2]^-$

In addition to the geometry of the complex, Vorob'ev-Desyatovskii et al. (2012) also proposed that the cyanometallate fixation occurs with a partial or complete dehydration of anions and that adsorption will decrease with an increase in the anion hydration energy. Yin et al. (2011) suggested the same theory and related the lower hydration state of linear $[Au(CN)_2]^-$ to be the reason for the gold selectivity over linear $[Ag(CN)_2]^-$ complexes. The reason for the lower adsorption of $[Pd(CN)_4]^{2-}$ than $[Pt(CN)_4]^{2-}$ is therefore related to the activated carbon being more selective for Pt, which in turn is hypothesized to be to a lower hydration energy for $[Pt(CN)_4]^{2-}$. According to Cortina et al. (1998) and Versiane and Ciminelli (2000), the hydration energy of anionic complexes depends on the charge density of the complex, meaning the ratio of charge to number of elements in the complex. The higher the ratio, the more water molecules are required to stabilize the anion in solution, and thus the more hydrated the complex. For cations, the hydration energy depends on the charge and radius of the cation with smaller cation radii resulting in larger hydration energies if the charge is equal (Wulfsberg, 1991). Since the charge density of $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ is the same, the atomic radii of Pt and Pd were therefore considered and since the Pt atomic radius is larger than that of Pd (Pt is situated below Pd on the periodic table) it is estimated that the hydration energy of $[Pt(CN)_4]^{2-}$ will most likely be smaller than that of $[Pd(CN)_4]^{2-}$. This hydration energy estimation method for Pt and Pd cyano complexes was checked against the thorough calculations and active measurements for $[Zn(CN)_4]^{2-}$ and $[Hg(CN)_4]^{2-}$ by Yin et al. (2011), who found that the hydration energy for $[Zn(CN)_4]^{2-}$ is larger than for $[Hg(CN)_4]^{2-}$ with the Zn atomic radius being smaller than that of Hg. A similar conclusion can be made for $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$. It is, however, proposed that this theory be verified by active measurements of the hydration energies for $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ complexes.

Considering that the typical loadings observed in gold plants range from 200 (Davidson and Baily, 1991) to 7000 mg/kg AC (Fleming et al. 2011, Laxen, 1984) and the potential of activated carbon to adsorb Pt from very dilute solutions (0.15 mg/L Pt and 0.38 mg/L Pd) (Mpinga, 2012), activated carbon does seem to be a viable process consideration for the upgrading of PGMs in a cyanide leach stream. The temperature, free cyanide and base metals as previously discussed, are important process variables, which will affect the PGM adsorption, and the influence of these factors on the adsorption rate and capacity is therefore discussed in the following sections.

4.1.3 Factors affecting adsorption*†

4.1.3.1 Temperature

Temperature is an important factor in the activated carbon process. In gold recovery, leaching and adsorption occur at ambient temperature, and elevated temperatures are used only in the stripping of the gold in the elution process. For Pt and Pd, leaching will typically take place at elevated temperatures, which can range from 55°C on heaps or in tanks (Eksteen et al. 2012) to between 120 and 180°C in autoclaves (Chen and Huang, 2006) with the leaching kinetics (and overall extraction) of Pt and Pd increasing with increasing temperature. It is, therefore, likely that any industrial process would operate at elevated temperatures. From the elution experiments, it was seen that significant elution of the PGMs already occurred at 60°C (to be discussed in more detail in the following section 4.2.1.1) and, as adsorption can be considered to be the reverse of the elution process (Van Deventer et al. 1994), it was deemed important to investigate the influence of temperature on the adsorption process to determine the degree of adsorption at elevated temperatures as well as to understand the role temperature plays in the process in more detail.

The influence on temperature was therefore investigated in a series of experiments similar to those completed by Mpinga et al. (2012). The first set of data derived from these experiments, as shown in Figure 4.33, compares the adsorption of the three precious metals in question at 25°C. Figure 4.33 shows that complete adsorption of the PGMs occurs within the first hour with the rate of adsorption of gold being considerably faster than the rate of adsorption of Pt and Pd. 97% of the gold adsorbed within the first 25 minutes compared to 64% for Pd and 66% for Pt for the same amount of time.

* Novel contribution – Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2014. The effect of temperature, cyanide and base metals on the adsorption of Pt, Pd and Au onto activated carbon, Hydrometallurgy, Vol 149, pp 132–142

† Cornelius A Snyders, Steven M Bradshaw, Guven Akdogan, Cleophace N Mpinga, Andries P Van Wyk, Jacques J Eksteen, 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. IMPC, Santiago, Chile, 20 -24 October 2014.

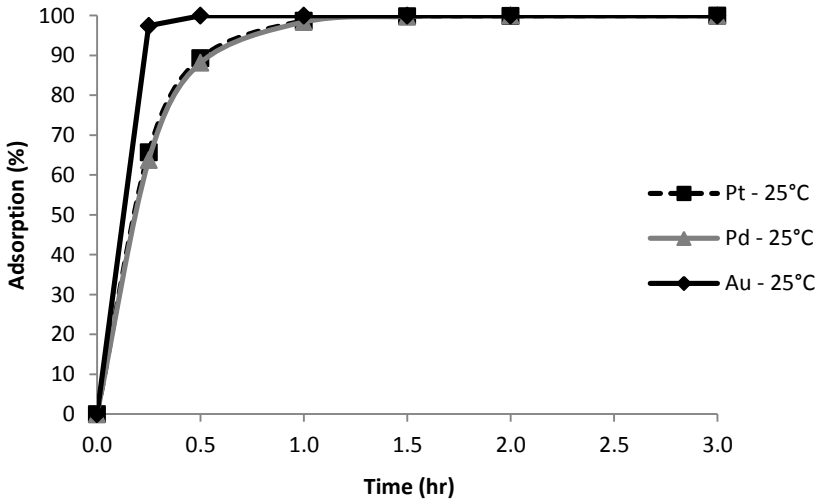


Figure 4.33: Adsorption of Pt, Pd and Au at 25°C in a stirred vessel, showing the faster adsorption kinetics for Au. (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

These adsorption rates shown in Figure 4.33 are, however, faster (99% Adsorption after 1 h) when compared to that generally found by Mpinga et al. (2012) who demonstrated adsorption of 92% Pt, 89% Pd and 98% Au in 1 h with the corresponding rate constants being 1.6 h^{-1} for Pd, 1.8 h^{-1} for Pt and 2.7 h-1 for Au calculated for the first two hours of adsorption with a first order model. The reason for the faster adsorption for this work is mainly attributed to the absence of base metals (10 mg/L for Ni and 10 mg/L Cu, Mpinga et al. 2012) in these solutions as well as the use of a stirred vessel instead of the traditional rolling bottle method, which has different mass transfer kinetics. Fleming et al. (2011) demonstrated that mixing is more efficient in a stirred tank than in the bottle roll tests and this translates to improved CIP or adsorption performance. To put these two different tests into perspective, Fleming et al. (2011) suggested that the kinetic performance that is achieved in large conventional CIP tanks is similar to that of a rolling bottle, while the performance of smaller, well-mixed tanks such as Pumpcells is better simulated by small laboratory stirred tanks In general, the rates of adsorption determined in this study, as well the adsorption rates determined by Mpinga et al. (2012), are fast due to the relatively high concentration (10 g/L) of virgin activated carbon used. Typical CIP adsorption is predominantly dominated by the slower rate of intraparticle diffusion that dominates after the first few hours the carbon spends in each tank indicating the necessity of performing experiments where the loading occur repeatedly onto the same carbon.

The comparison of the adsorption between gold, platinum and palladium at higher temperatures, is similar to that at room temperature (Figure 4.33) and the results at 35°C and 50°C are shown in Figures A2 and A3 in Appendix A. More importantly and more towards the aim of this study is the comparison between the adsorption of the specific metals at different temperatures. These results are shown in Figure 4.34 to Figure 4.36.

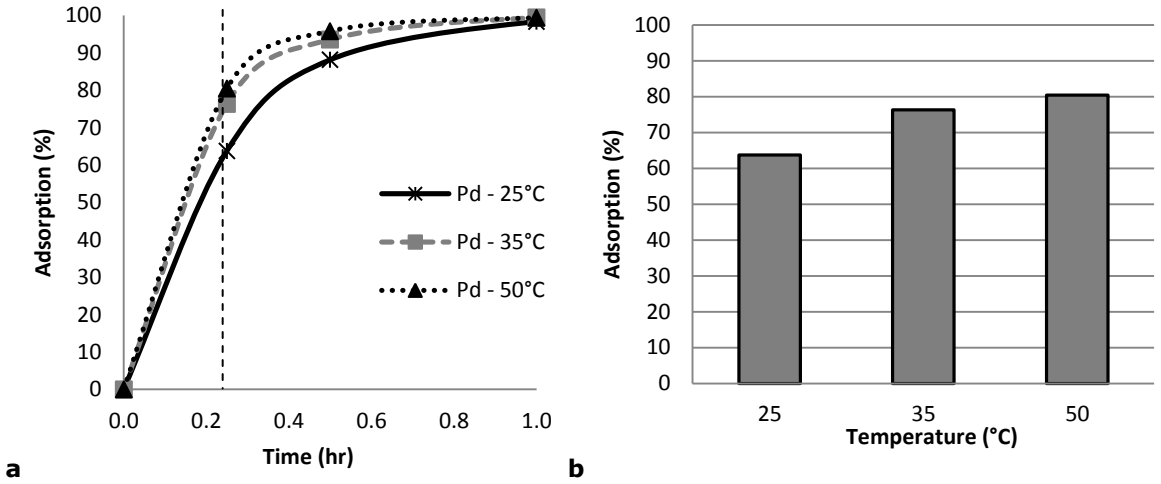


Figure 4.34: a) Adsorption of Pd over time at different temperatures and b) the difference in adsorption with an increase in temperature at 25 min. (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

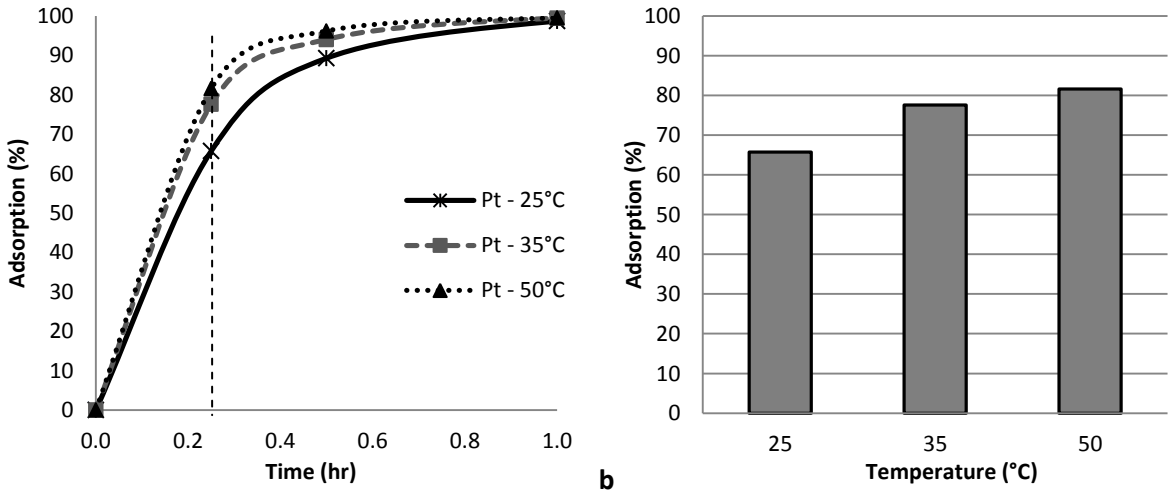


Figure 4.35: a) Adsorption of Pt over time at different temperatures and b) the difference in adsorption with an increase in temperature at 25 min. (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

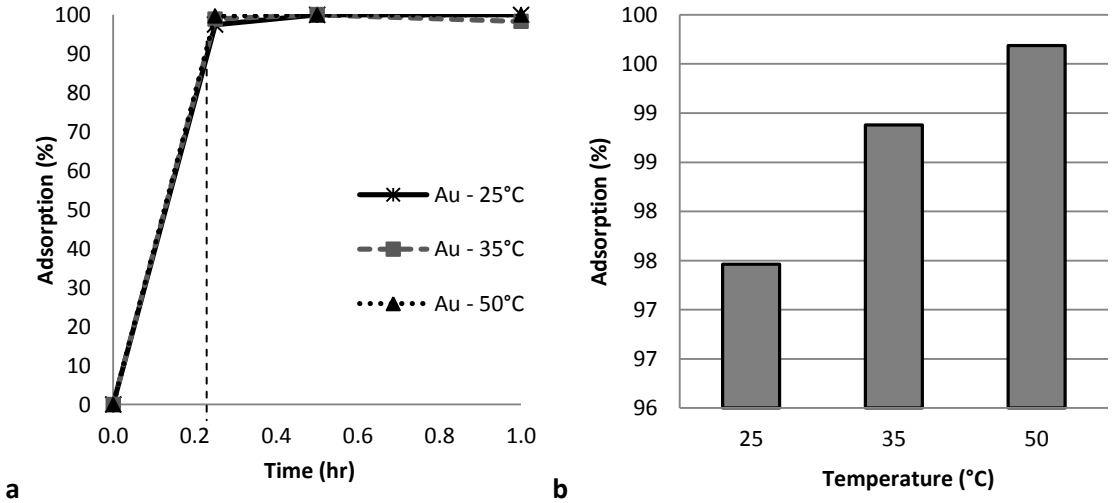


Figure 4.36: a) Adsorption of Au over time at different temperatures and b) the difference in adsorption with an increase in temperature at 25 min. (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

An increase in the rate of adsorption with temperature was seen for all three metals, as shown in Figure 4.34 to Figure 4.36. Although all metals were adsorbed after one hour, the difference in adsorption for Pt (Figure 4.35) and Pd (Figure 4.34) after 25 minutes of adsorption was almost 20% more at 50°C than at 25°C. For Au adsorption (Figure 4.36) an increase in the rate of adsorption with increasing temperature also occurred ,but the effect was substantially reduced and after 25 min, the adsorption at 25°C was 95% compared to 100% at 50°C. This may indicate that the effect of temperature on the rate of gold loading is either much less than for platinum or palladium or that the real effect is simply obscured by the lack of data points between 0 and 25 minutes.

For further analysis, reaction rates were determined by plotting ln[Pt, Pd, Au] vs time (Figure 4.37 to Figure 4.39) to reveal a straight line with a slope (-k) equals to the reaction rate according to equation 4.2 (Steinfield et al. 1998, Fuerstenau et al. 1987, Fleming and Nicol, 1984). The slowest rate of adsorption was found to be for Pd at 25°C, which reached 100% adsorption after two hours and the fastest rate of adsorption was for Au at 50°C, which was 100% adsorbed after only 25 min. As soon as 100% adsorption was reached, the first order model (Eq. 4.2) did not apply anymore and the data points beyond this point were therefore not taken into consideration (Feurstenau et al. 1987).

$$\ln[PGM] = \ln[PGM_0] - kt \qquad (4.2)$$

PGM = [Pt], [Pd], [Au]

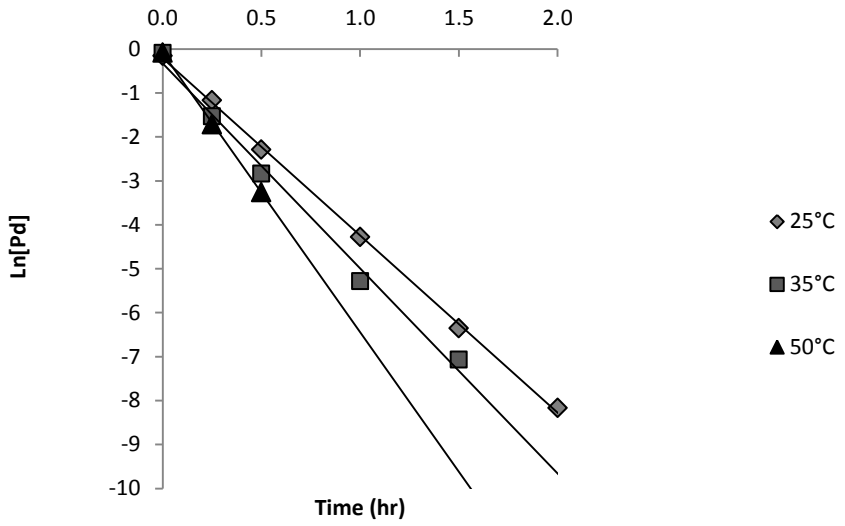


Figure 4.37: The effect of temperature on the rate of Pd adsorption (R^2 > 0.992) (pH = 9.5, BM = 0, NaCN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

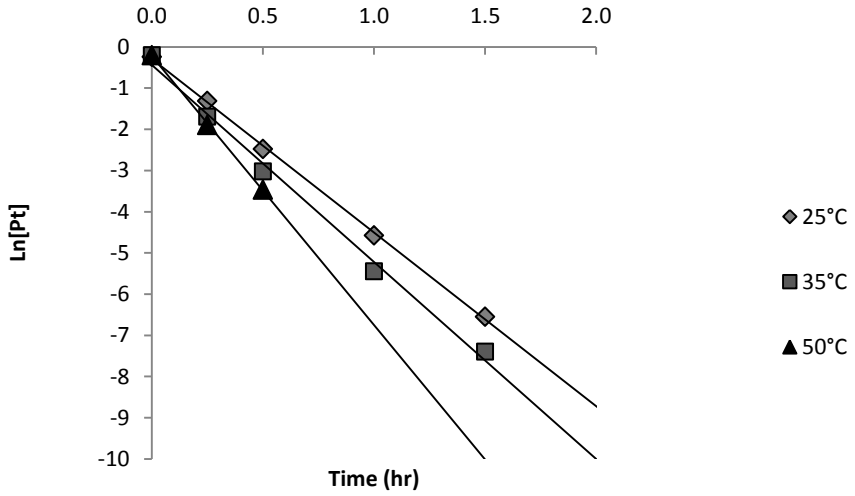


Figure 4.38: The effect of temperature on the rate of Pt adsorption (R^2 > 0.994) (pH = 9.5, BM = 0, NaCN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

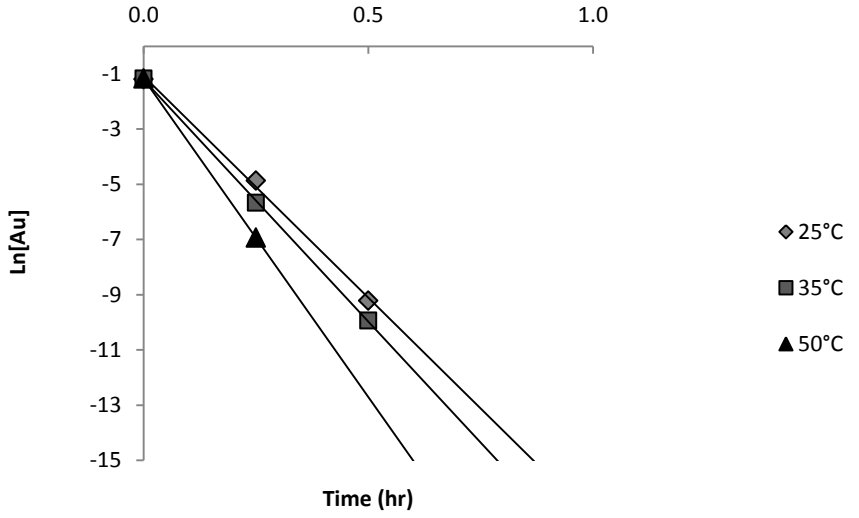


Figure 4.39: The effect of temperature on the rate of Au adsorption (R^2 > 0.997) (pH = 9.5, BM = 0, NaCN = 0, AC = 10 g/L, PGMs: Pt = 0.15mg/L, Pd = 0.38 mg/L, Au = 0.1 mg/L)

From the Arrhenius plot (Figure 4.40) the activation energy (E_{act}) could be calculated and is shown in Table 4.25. Figure 4.40 also clearly indicates the higher rate of adsorption for gold, while the marginally lower slope of the graph (smaller activation energy E_{act}) indicates a lesser dependence on temperature.

Table 4.25: Calculated activation energies for Pd, Pt and Au

	E_{act}	k (h^{-1})		
	kJ/mol	25°C	35°C	50°C
Pd	14.7	4.0	4.7	6.4
Pt	14.2	4.2	4.8	6.5
Au	11.8	16.0	17.5	23.1

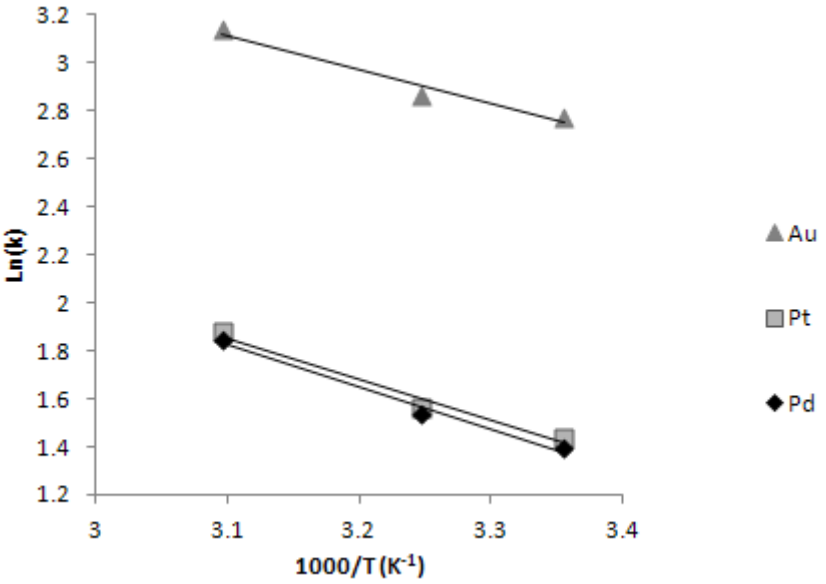


Figure 4.40: An Arrhenius plot to indicate the effect of temperature on the adsorption of Pd, Pt and Au (R^2 > 0.96) (pH = 9.5, BM = 0, NaCN = 0, AC = 10 g/L, PGMs: Pt = 0.9 mg/L, Pd = 1.0 mg/L, Au = 0.2 mg/L)

The increase in adsorption rate with temperature is similar to that found by Fleming and Nicol (1984), Fuerstenau et al. (1987) and Ladeira et al. (1993) and the calculated activation energy for Au of 11.8 kJ/mol (2.8 kcal/mol) corresponds well to the gold activation energy of 2.6, 2.0 and 2.4 kcal/mol calculated respectively by these authors. The low activation energies are indicative of a diffusion controlled process (Meng and Hang, 1993, Steinfield et al. 1998, Atkins and de Paula, 2006, Ladeira et al. 1993, Fuerstenau et al. 1987, Fleming and Nicol, 1984, Al-Ghouti et al. 2005) with Al-Ghouti et al. (2005) using an activation energy value of 42 kJ/mol as a guideline to distinguish between diffusion controlled processes and chemically controlled processes. The finding of diffusion control also corresponds to the increase in loading kinetics from the rolling bottle method to a stirred vessel as discussed previously in this section. (Ladeira et al. 1993). The plot of In [PGM] versus t (Eq. 4.2) yielding a straight line (Figure 4.37 to Figure 4.39) points to a film diffusion controlled process for these experiments (Fuerstenau et al. 1987), while particle diffusion has been ruled out, due to the low PGM concentration (Fleming and Nicol, 1984) and the intra particle diffusion plot (Eq. 4.3, Vimonses et al. 2009) that could not be fitted to the data. Ruthven (1984), however, stated that it is not always possible to categorize a particular system unequivocally and that many intermediate cases exist. This seems to be applicable to this case as well when considering Mpinga et al. (2013), who found that Pt and Pd exhibit pseudo-second order kinetics and suggested that the rate-limiting step may be chemical adsorption. Although the second order model results in a good mathematical fit over the entire data range in this case, it also predicts, according to the constants calculated from the data, that the equilibrium adsorption for Au is less than for Pt and Pt less than Pd, which is not a true representation of what occurs. According to the second order model (Appendix D), the equilibrium adsorption will be the highest at the lowest temperature, which is also not consistent with experimental results and it was ultimately concluded that for these experiments, the first order model resulted in a better representation of the data than the pseudo-second order model.

$$q_t = k_{id} t^{1/2} + C_{id} \quad (4.3)$$

q_t = PGMs adsorbed after a time t,
k_{id} = intraparticle diffusion rate constant (mg/g $min^{1/2}$)
C_{id} = the thickness of the boundary layer.

In addition to an increase adsorption rate, literature suggests that the equilibrium loading, however, will decrease as the temperature increases. Based upon this, the effect of temperature on the continuous adsorption of activated carbon was therefore investigated.

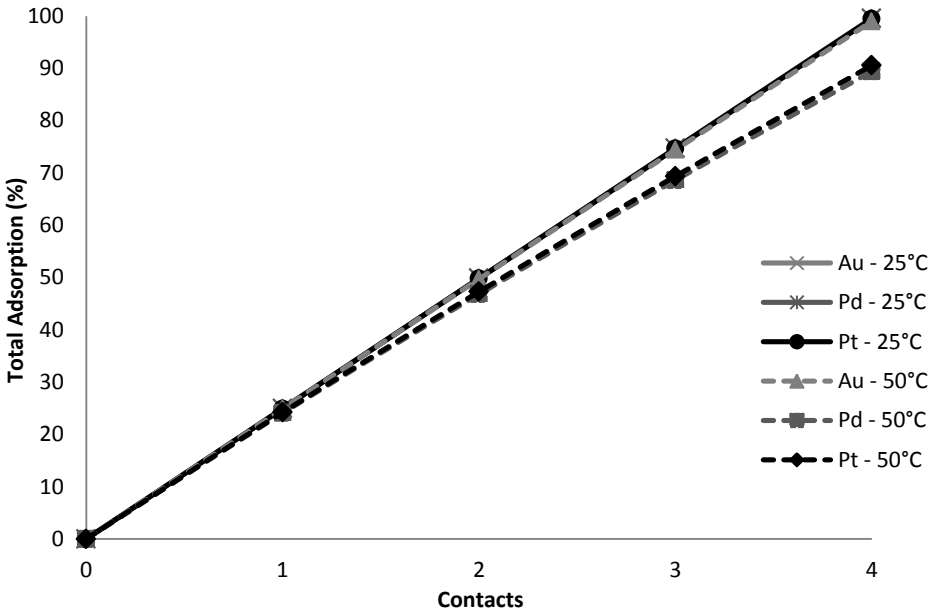


Figure 4.41: The effect of temperature on the PGM adsorption after consecutive loading from a pregnant PGM leach solution. (0 NaCN, pH = 9.5, BM = 0, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L)

Figure 4.41 shows the effect that temperature has on the adsorption of Pt, Pd and Au onto activated carbon after 4 consecutive 2-hour loadings. For the first contact, the loadings for Pt, Pd and Au at 25 and 50°C were identical. This first contact corresponded to the adsorption found by the previous set of experiments (Figure 4.34 to Figure 4.36), which indicated complete adsorption of the PGMs at 25 and 50°C after 1 hour of adsorption. From contact 2 and onwards, the adsorption of Pt and Pd at 50°C started decreasing, with the effect becoming greater towards contact nr 4. At the end of contact nr 4, 99% of the total amount of platinum and palladium adsorbed at 25°C compared to 91% of the platinum and 89% of the palladium at 50°C. The behaviour of platinum- and palladium cyanide, which shows an increase in adsorption kinetics with an increase in temperature, but a decrease in total amount adsorbed, therefore corresponds to the behaviour of gold cyanide adsorption at different temperatures as described by Fleming and Nicol (1984) and Ladeira et al. (1993). The similar behaviour of Au and Ag is related to the equilibrium loading being exothermic in nature (McDougal et al. 1980, Fleming and Nicol, 1984, Cho and Pitt, 1979) and the equilibrium therefore shifting to the reverse reaction (desorption) as the temperature increases.

No difference can be seen between the adsorption of gold cyanide at 25 and 50°C after 4 contacts and corresponds to the lower activation energy of Au adsorption, which means a lesser dependence on temperature. Four contacts are therefore probably not enough to show the difference between these temperatures for gold adsorption. The findings of Fleming and Nicol (1984) related to significantly higher gold tenors (25 mg/L Au in solution) than in the current work (0.22 mg/L), which resulted in significantly higher activated carbon loadings. The reason for gold adsorption being less affected by temperature than platinum and palladium is related to the affinity of activated carbon towards these metals ions with the selectivity sequence expressed by Mpinga et al. (2014) to be:

$$Au(CN)_2^- > Pt(CN)_4^{2-} > Pd(CN)_4^{2-} > Ni(CN)_4^{2-} > Cu(CN)_3^{2-}$$

Vorob'ev-Desyatovskii et al. (2012) attributed this selectivity sequence to the shape of the molecule as discussed in section 4.1.1.

4.1.3.2. Cyanide concentration

Previously it has been reported by Mpinga (2012) that no significant difference was found in the adsorption of PGMs with a variation in cyanide concentration from 100 to 300 mg/L. Under continuous loading conditions, the effect of cyanide, however, does become more pronounced as shown in Figure 4.42.

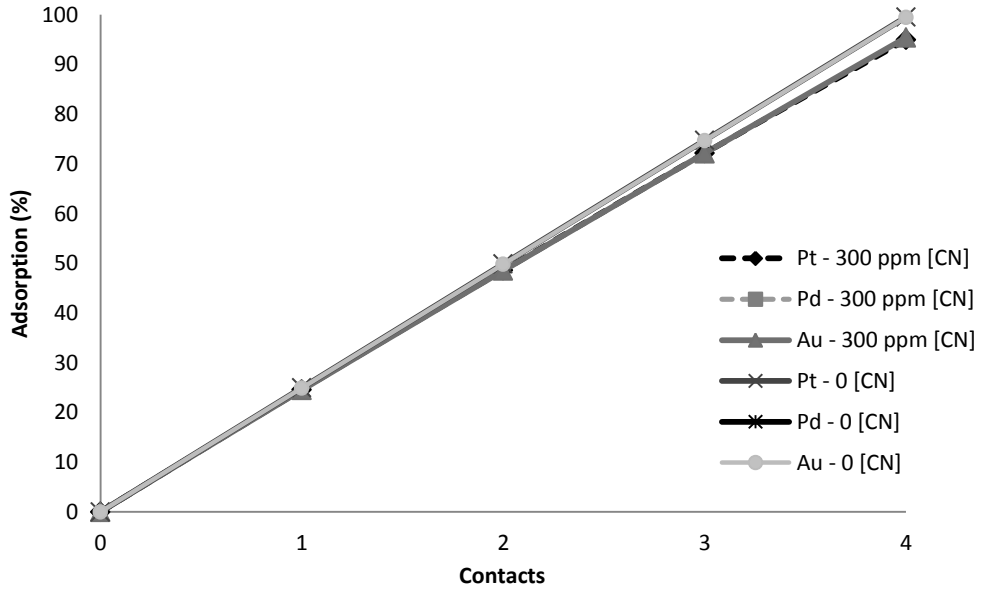


Figure 4.42: The effect of cyanide concentration on the PGM adsorption after consecutive loading from a pregnant PGM leach solution. (25°C, pH = 9.5, BM = 0, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L)

The effect of cyanide concentration is very similar to that of temperature and can be seen in Figure 4.42. As previously mentioned and as expected, the effect of cyanide concentration on the adsorption of platinum and palladium becomes apparent after consecutive loadings with the effect increasing with each contact. At the end of contact nr 4, 99% of the total amount of platinum and palladium adsorbed with no cyanide present compared to 95% of the platinum the palladium with 300 mg/L of added cyanide. The decreasing effect of free cyanide on the adsorption of gold is well

known and has been reported on by numerous authors (Van Deventer, 1984, Woollacott and Guzman, 1993, Nicol et al. 1984, Davidson et al. 1982)

4.1.3.3 Temperature and cyanide concentration

Continuing from the previous two sections; it was seen that, similar to the effect of temperature, the effect of cyanide on the adsorption of platinum and palladium became more pronounced after consecutive loadings with the effect increasing with each contact. By evaluating the total amount of adsorption after the four contacts, it can be seen that at the end of contact 4 (Figure 4.42), 99% of the total amount of platinum and palladium adsorbed when no cyanide was present compared to 95% adsorption when 300 mg/L of cyanide was added. At a higher temperature of 50°C, 90% of the Pt and Pd adsorbed with no cyanide addition compared to only 72% adsorption with 300 mg/L cyanide. When the temperature was increased to 50°C, the difference in Pt and Pd adsorption between 0 and 300 mg/L cyanide addition, therefore increased approximately four times from a 4 pp difference to an 18 pp difference (Figure 4.43). The gold adsorption was influenced similarly (Figure 4.43), but to a much lesser extent and was reduced by only 0.3 pp with an increase in cyanide from 0 to 300 mg/L at 25°C, but the reduction in adsorption also increased by four times to 1.2 pp at 50°C. This decreasing effect on the adsorption of Au as the cyanide increases, and which is enhanced when the temperature is increased, has also been discussed by Van Deventer (1984). Van Deventer and Van der Merwe (1994b) and Adams and Fleming (1989) stated that cyanide reacts with the functional groups on the carbon surface and essentially passivizes the carbon surface for the adsorption of metal cyanide complexes. The degree of passivation is determined by the cyanide concentration and the temperature.

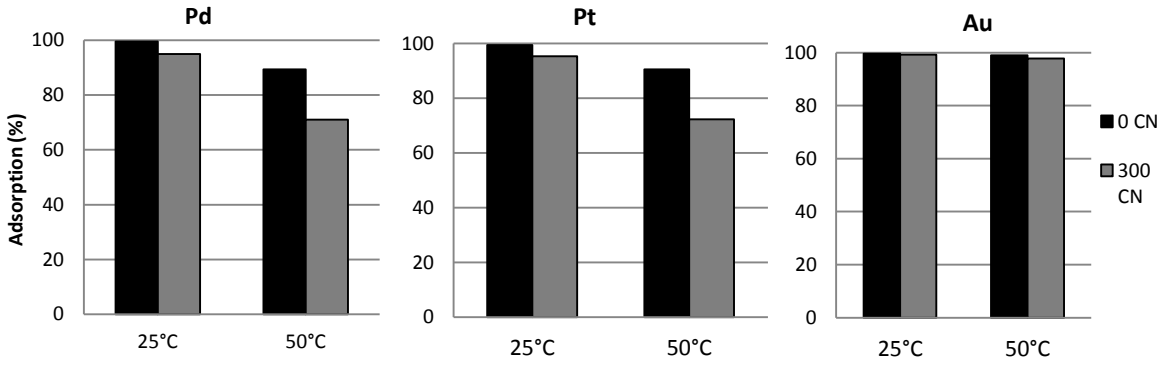


Figure 4.43: The effect of temperature and cyanide on the total adsorption of Pt, Pd and Au after 4 consecutive loadings from a pregnant PGM leach solution. (pH = 9.5, BM = 0, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L)

4.1.3.4 Base Metals

Mpinga (2012) found that Ni adsorption exhibits kinetics similar to those of Pt, Pd and Au and ascribed the high initial uptake rate of $[Ni(CN)_4]^{2-}$ (planar) to the availability of a large number of adsorption sites on the adsorbent surface. Marsden and House (2006) observed that, despite the highly selectivity of activated carbon for gold and silver over most other metal species, high

loadings of non precious metals can be achieved onto activated carbon in the absence of significant precious metal values.

Mpinga (2012) also found that after one hour of adsorption, Cu adsorption was roughly 5% (90 mg/kg AC loading), whilst Pt extraction was between 95 to 100% (15 mg/kg AC loading). Cu co-extraction might therefore be reduced by minimizing the residence time during adsorption. The copper adsorption increased considerably over time from 5% after one hour to between 85 and 90% after 72 hours (Mpinga (2012). According to Boshoff (1994), Adams (1991) and Lu et al. (2002), copper adsorption depends on the copper cyanide complex present, which is determined by the solution conditions such as pH, temperature and mole ratio of copper to cyanide. A general guideline is that $[Cu(CN)_2]^-$ adsorbs strongly and is favoured at low pH values, low copper concentrations and low cyanide concentrations, whereas $[Cu(CN)_4]^{3-}$, which adsorbs very little and is formed at pH values above 10 and cyanide concentrations above 200 mg/L. $[Cu(CN)_3]^{2-}$ is the most stable form of copper cyanide and is usually the dominant complex found in typical plant solutions. Souza et al. (2014) found that at a pH of 10.5 and a CN/Cu molar ratio of 2.5, the $[Cu(CN)_2]^-$ species are stable and present. It was also observed that from a CN/Cu molar ratio of 4 at pH 10.5, the formation of the $[Cu(CN)_4]^{3-}$ species gradually increases as the CN/Cu molar ratio increases, while the amount of $[Cu(CN)_3]^{2-}$ species gradually decreases. At a CN/Cu molar ratio of 10, only the $[Cu(CN)_4]^{3-}$ species were observed. Due to the relatively low amount of free cyanide present in the experimental work performed by Mpinga et al. (2014) (12 mg/L free CN^- and 19 mg/L Cu^+), it was expected that a mixture of $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ was present.

The effect of base metals on the adsorption of platinum, palladium and gold after consecutive loadings, as determined during this study in the absence (no free NaCN) and presence (300 mg/L NaCN) of cyanide, is shown in Figure 4.44 and 4.45.

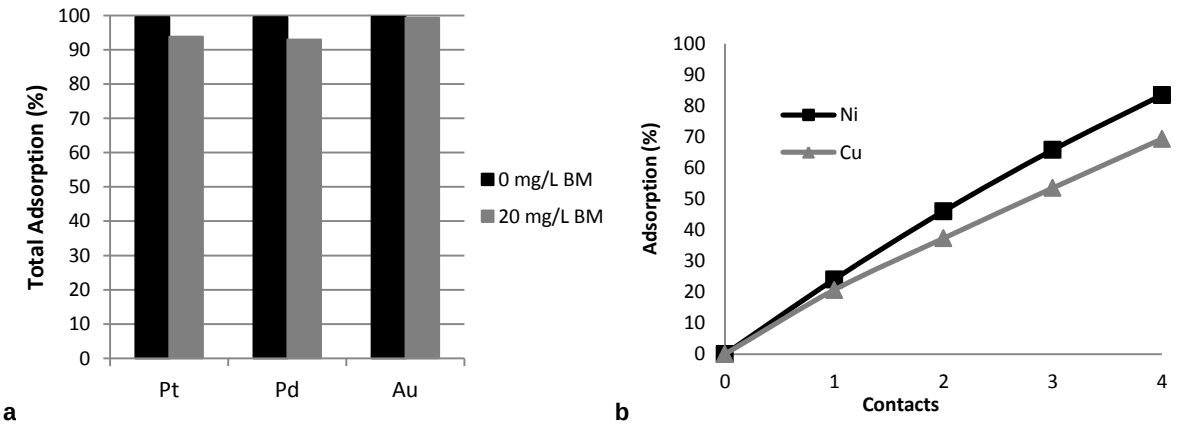


Figure 4.44: a) The effect of the presence of base metals (Cu and Ni) on the total adsorption of Pt, Pd and Au after 4 consecutive loadings from a pregnant PGM leach solution with b) the corresponding Cu and Ni (NaCN = 0 mg/L, pH = 10.5, Cu = 10 mg/L, Ni = 10 mg/L, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L, Temperature = 25°C)

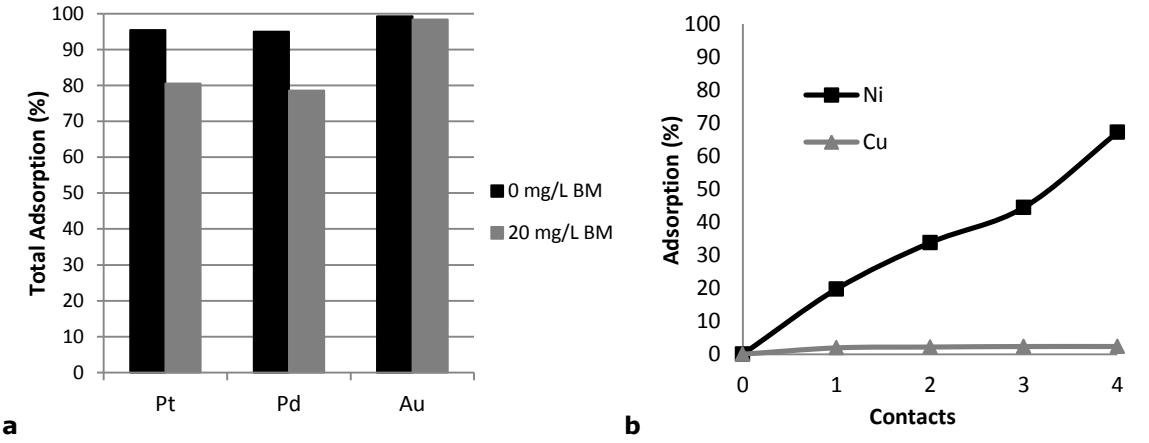


Figure 4.45: a) The effect of the presence of base metals (Cu and Ni) on the total adsorption of Pt, Pd and Au after 4 consecutive loadings from a pregnant PGM leach solution with b) the corresponding Cu and Ni adsorption (NaCN = 300 mg/L, pH = 10.5, Cu = 10 mg/L, Ni = 10 mg/L, Pt = 0.9 mg/L, Pd = 0.2, Au = 0.2 mg/L, Temperature = 25°C)

From the experimental data shown in Figure 4.44 it is seen that the presence of base metals has a significant effect on Pt and Pd adsorption. Both Pt and Pd adsorption was reduced by 7 percentage points (pp) when base metals were present in the absence of NaCN, while the deleterious effect on Au adsorption was again found to be less significant at these specific conditions (Figure 4.44a). The impact on the PGM adsorption by the BMs seems small considering the BMs are present in much higher concentration than the PGMs. This is related to the higher selectivity of activated carbon towards PGMs as indicated by the adsorption selectivity order given in section 2.44. The impact also increases sharply with each contact with >98.6% (calculated with Eq. 3.1) of the Pt and Pd adsorbing in the first contact, which decreases to 86% adsorption (Eq. 3.1) for contact 4 and resulting in the total adsorption (calculated with Eq. 3.2) of 93% for all four contacts as indicated in Figure 4.43a. The Au adsorption is even less affected due to the Au taking up sites first on the activated carbon (Yin et al. 2011). Both Ni and Cu were adsorbed according to Figure 4.44b with the low CN/Cu ratio and the pH of 9.5, pointing to $[Cu(CN)_2]^-$ (Souza et al. 2014).

When both cyanide and base metals were present (Figure 4.45a) Pt and Pd adsorption reduced by 15 pp. From Figure 4.45b, it can be concluded that in the case when cyanide was present, it was mainly the nickel in the solution that contributed to the reduction in PGM adsorption and not the copper, as almost no copper (2.3% adsorption resulting in a loading of 101 mg/kg) compared to a significant quantity of nickel adsorption (67% resulting in a loading of 2153 mg/kg). The reason for the low copper adsorption is ascribed to the high cyanide content resulting in the formation of predominantly poorly adsorbing $[Cu(CN)_4]^{3-}$ complexes, while the high Cu adsorption in the case of no cyanide addition is due to the formation of the strongly adsorbed $[Cu(CN)_2]^-$ complex. This is in agreement with Clark et al. (1986) who, through infrared spectroscopy, found that when copper was adsorbed onto charcoal as CuCN originally (similarly to this study), it disproportionated to $[Cu(CN)_2]^-$ and Cu^+, (Cu^+ being bound by a surface hydroxide group) with $[Cu(CN)_2]^-$ being the major specie present. In the presence of free cyanide, it was found that both adsorbed species converted to $[Cu(CN)_3]^{2-}$.

Ni adsorption, as opposed to Cu adsorption, seemed to be less influenced by the cyanide concentration with Fisher and LaBrooy (1997) finding the Ni adsorption remained unchanged as the cyanide concentration varied from 250 to 500 mg/L. Although this study did not find the nickel adsorption to be unaffected by an increase in free cyanide (as shown in Figure 4.46a), the effect is still significantly less (16 pp difference) when compared to the presence of cyanide (0 and 300 mg/L CN) during copper adsorption, which results in a 67 pp difference in copper adsorption according Figure 4.46b

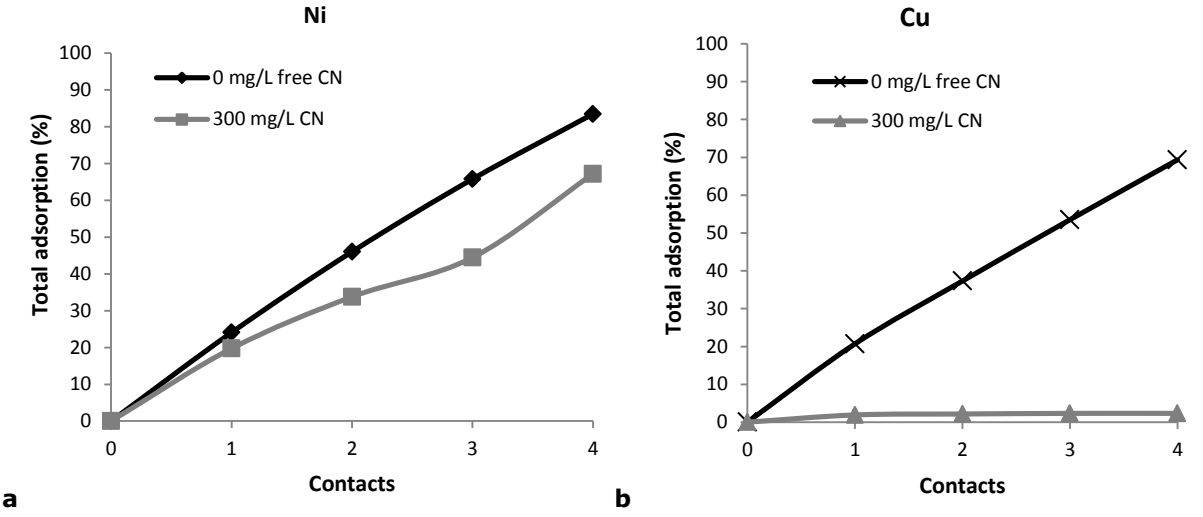


Figure 4.46: The effect of cyanide on the BM adsorption after consecutive loading from a pregnant PGM leach solution. (23°C, pH = 9.5, Cu = 10mg/L, Ni = 10mg/L, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L, Temperature = 25°C)

It has been shown sufficiently that the presence of both copper and nickel adsorption impairs PGM adsorption. Experimentation from this study (Appendix A, Figure A.114) also indicated that the initial rate of Pt adsorption is dramatically reduced in the presence of copper when loading from a higher initial solution concentration of 5 mg/L Pt, while that of gold remains almost unchanged.

An important conclusion is, therefore, the presence of nickel and copper (especially when in the $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ co-adsorbing forms) in the adsorption circuit will have a larger impact on the adsorption of platinum and palladium than on the adsorption of gold and need to be carefully taken into consideration with the design of the PGM adsorption circuit to ensure sufficient PGM recovery. Removal of these metals before the adsorption stage is recommended.

4.1.3.5 Temperature and Base Metals

The negative effect of temperature, cyanide and base metals individually on the adsorption of platinum, palladium and gold has been established. It has also been established that the detrimental effect of cyanide will increase as the temperature increases. Since Cu and Ni adsorption is vastly different from each other in terms of rate of adsorption and quantity adsorbed, it first has to be established what the effects of temperature and cyanide are on the adsorption of the base metals individually in order to understand the combined effect of temperature and base metals as well as the combined effect of cyanide and base metals on the adsorption of PGMs. The base metal adsorption after the 4 consecutive loadings can be seen in Figure 4.47. Ni adsorption

follows a similar trend as that of Pt and Pd adsorption with the Ni adsorption decreasing with increasing temperature and cyanide addition and this effect increasing at both higher temperatures and cyanide addition as discussed in section 4.1.2.3.

The copper adsorption in Figure 4.47b follows the trend with cyanide as explained in the previous section 4.1.2.4 and indicates 70% and 80% adsorption with no free cyanide addition and almost no adsorption in the presence of 300mg/L cyanide at 25°C and at 50°C. When the adsorption at 25°C and 50°C with no free cyanide is compared, it is interesting to note that the total copper adsorption after 4 contacts increases with temperature. This is speculated to be due to the increase in the kinetics of adsorption as the temperature increases as discussed for Pt, Pd and Au in section 3.2 above. As the copper adsorption is probably not close to equilibrium loadings (plant adsorption copper loadings, which are normally significantly lower than equilibrium loadings, as high as 30000 mg/kg carbon recorded, Fleming and Nicol, 1984), the faster kinetics of adsorption resulted in more copper being adsorbed within the same amount of time. An alternative explanation is simply that the ratio of the stronger adsorbing $[Cu(CN)_2]^-$ to the less adsorbing $[Cu(CN)_3]^{2-}$ is higher when the temperature is increased and subsequently results in more copper being adsorb at 50°C. According to Lu et al. (2002), the ratio of $[Cu(CN)_2]^-$ to $[Cu(CN)_3]^{2-}$ below a CN:Cu mole ratio of three does not change as the temperature increases from 25°C to 60°C, but above a CN:Cu mole ratio of three, the lower coordinated complex is favoured when the temperature is increased to 60°C. Lu et al. (2002) ascribed this effect due to the decrease in the stability constants of copper cyanide complexes, but did not elaborate on the matter. As this was not the main aim of this research project, this was not further investigated.

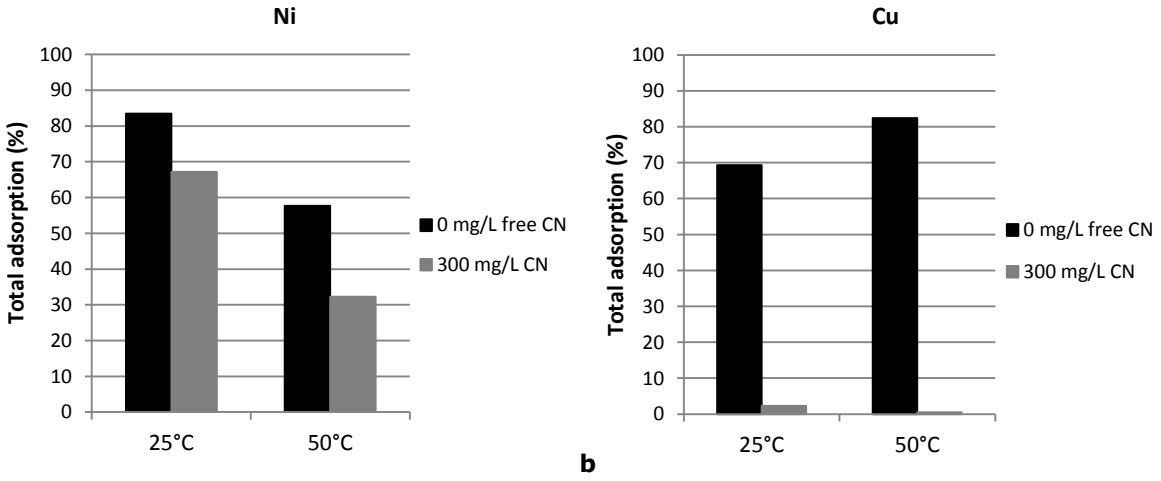


Figure 4.47: The effect of temperature and cyanide on a) the nickel and b) copper adsorption after consecutive loading from a pregnant BM and PGM leach solution. (25°C, pH = 9.5, Cu = 10 mg/L, Ni = 10 mg/L, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L)

To interpret the change in PGM adsorption due to the presence of base metals, the quantity of base metals adsorbed, which actively take up sites on the activated carbon in the place of PGMs, was calculated and can be seen in Table 4.26.

Table 4.26: Quantity of base metals adsorbed at various cyanide and temperature levels.

Run	[CN]	Temperature	Adsorption		
			Ni	Cu	Total
	mg/L	°C	mg	mg	mg
1	**0**	**25**	25	12	37
2	**300**	**25**	22	1	23
3	**0**	**50**	18	18	37
4	**300**	**50**	10	0.2	10.2

According to Table 4.26, Ni loadings decreased slightly with an increase in cyanide at both 25°C and at 50°C, while copper adsorption decreased to basically no adsorption at high cyanide levels and ultimately resulted in a total decrease in base metals adsorbed. At low cyanide levels, Ni adsorption decreased with the increasing temperature, but the copper adsorption increased, resulting in the total base metals adsorbed to be similar (nr 1 and 3 in Table 4.26). At high cyanide levels very little copper adsorption was taking place and the total base metals adsorbed therefore decreased with temperature, because the amount of Ni that was adsorbed, decreased.

The PGM adsorption at a high cyanide level, but at the different temperatures and in the presence of base metals, is shown in Table 4.27. At 25°C, the presence of base metals decreases the adsorption of palladium by 16 pp while at 50°C, only by 11 pp, This is ascribed to the lower amount of base metals, that were adsorbed (run 2 compared to run 4 as per Table 4.26) at the higher temperature. The decrease in platinum adsorption due to base metals was 15% at 25°C and 14% at 50°C while for gold it slightly increased from 1% to 3%.

At a low cyanide level, where the total amount of base metals adsorbed, was the same at 25°C and 50°C (nr 1 and 3 in Table 4.26), the detrimental effect of base metals on the adsorption of Pd increased from 7% to 13% when the temperature was increased. Pt adsorption followed this trend, but to a much lesser extent and only increased from 6% to 8% as the temperature increased.

In general, it is rather difficult to come to a definite conclusion regarding the combined effect of base metals and temperature on the adsorption of Pt, Pd and Au. It can rather be concluded that temperature, the free cyanide, as well as the time of the adsorption will contribute to the Cu and Ni adsorption independently, which in turn will determine the amount of these base metals, that will take up sites on the activated carbon and compete with the PGM adsorption.

Table 4.27: The effect of temperature and base metals on the total adsorption of Pt, Pd and Au after 4 consecutive loadings from a pregnant PGM leach solution. (pH = 9.5, Pt = 0.9 mg/L, Pd = 0.2 mg/L, Au = 0.2 mg/L)

	High cyanide – 300 mg/L			
	Temperature (°C)	**0 BM**	**20 BM**	**Difference (pp)**
Pd (adsorption %)	**25**	95	79	16
	50	71	60	11
Pt (adsorption %)	**25**	95	81	15
	50	72	58	14
Au (adsorption %)	**25**	99	98	1
	50	98	95	3
	Low cyanide – 0 mg/L			
	Temperature (°C)	**0 BM**	**20 BM**	**Difference (pp)**
Pd (adsorption %)	**25**	100	93	7
	50	89	76	13
Pt (adsorption %)	**25**	99	94	6
	50	91	83	8
Au (adsorption %)	**25**	100	99	0.2
	50	99	99	0.3

4.2 Elution Results*

The very first question that needed answering, is whether platinum and palladium will elute from activated carbon in a manner similar to gold. This is answered in Figure 4.48, which illustrates the elution of platinum, palladium and gold from activated carbon with 80°C distilled water and pre-treated with a caustic cyanide solution as outlined in the previous section. At first glance, a typical elution profile can be seen for platinum and palladium with a peak in concentration around 2 bed volumes for both platinum and palladium indicating fast elution kinetics for both metals. In comparison with platinum and palladium, the elution of gold was found to be significantly slower with less of a pronounced peak than that of platinum and palladium.

* Novel contribution - Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. South African Journal of Mining and Minerals. Vol 113. May 2013. pp 381 - 388

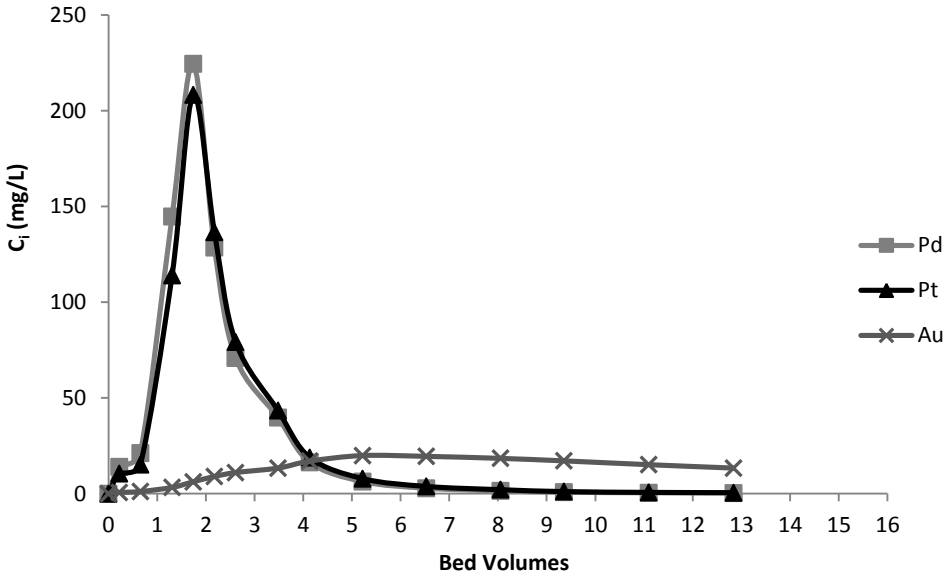


Figure 4.48: The elution of platinum, palladium and gold from activated carbon (650g/t of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.6% NaOH) at an elution temperature of 80°C.

The elution of platinum and palladium slows down significantly after approximately 4 – 5 bed volumes with the concentration of these metals in the eluate approaching 0, indicating that the carbon is either stripped completely or stripped of all elutable species. The gold elution profile, with a peak at approximately 5 to 6 bed volumes, with still a significant amount of gold on the carbon at 16 bed volumes, compares reasonably well with the shape of the elution profiles at this temperature found in literature and shown in Figure 2.4 (Van der Merwe, 1991) For higher gold recoveries, significantly higher temperatures are required. Upon designing of a continuous elution procedure for example, Riley (1991) found that a minimum of 95°C is necessary for efficient elution (95% recovery) and that recovery of gold decreases rapidly at lower elution temperatures to around 25% at temperatures between 85 and 90°C. It was also found that to achieve the 95% recovery at 95°C, a minimum cyanide level of 0.5% was required in the pre-treatment solution.

4.2.1 Factors affecting elution

4.2.1.1 Elution Temperature*†

Two sets of experiments were completed to investigate the effect of temperature. The first set was completed at 60, 80 and 95°C in glass elution columns at atmospheric pressure, while the second set of experiments was completed at 100 to 130° in a stainless steel pressurised column.

* Novel contribution - Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. South African Journal of Mining and Minerals. Vol 113. May 2013. pp 381 - 388

† Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

Glass column elutions

For Figure 4.49 and Figure 4.50 higher peak concentrations and a shift of the elution profiles towards the left of the graph indicate better elution efficiencies for platinum and palladium (Figure A.118 in Appendix A) at higher temperatures. The result is as expected and a similar profile can be seen for gold in Figure 4.51a and b. Industrial scale gold elution typically takes place at temperatures between 110 to 130°C. Costello (2004) found that for the elution of silver cyanide complexes from activated carbon in the temperature range 90 to 130°C the elution recoveries decreased and related this phenomenon to decomposing of the silver cyanide complexes with either AgCN or Ag forming on the activated carbon and which is not elutable under standard AARL conditions. A similar result was found by Jeffrey et al. (2009) for the elution of mercury from activated carbon, who found lower recoveries as the temperature increased from 110 to 160°C. As $Pd(CN)_4^{2-}$ only starts decomposing at temperatures around 150°C and $Pt(CN)_4^{2-}$ at 160 to 170°C (Chen and Huang, 2006), this result is not expected for Pt and Pd elution, but might be considered if a decrease in elution is seen with higher temperatures.

It is interesting to note that the effect of temperature is less pronounced for platinum when less cyanide is used in the pre-treatment step (Figure 4.50). This effect is most probably coupled with the less efficient elution, that is seen when less cyanide is used in the pre-treatment step. A more detailed discussion will follow in the pre-treatment section.

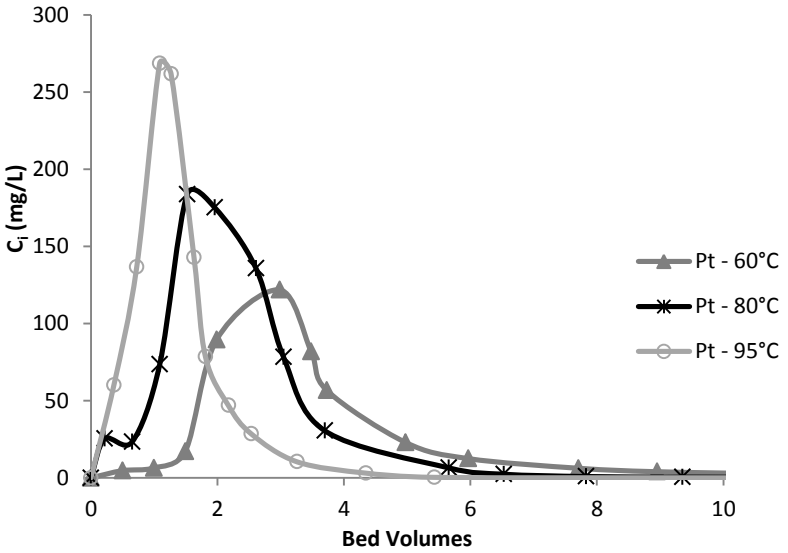


Figure 4.49: The effect of temperature on the elution of platinum with 2 % NaCN pre-treatment. (0.6% NaOH, 650g/t of Pt)

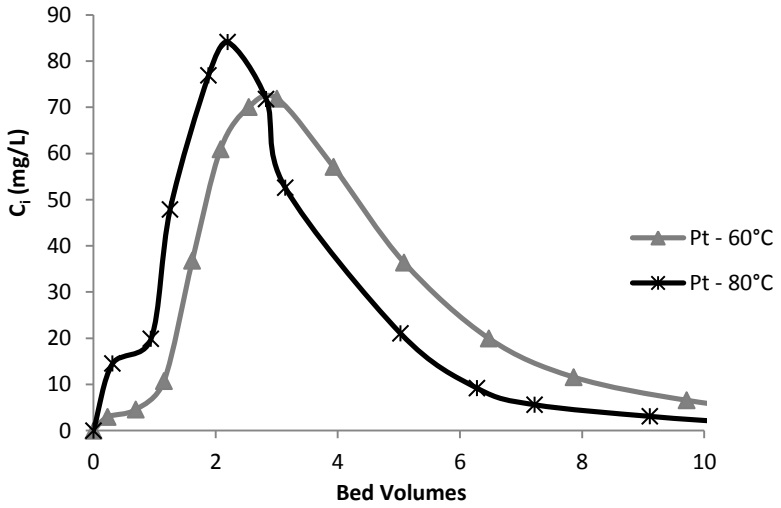


Figure 4.50: The effect of temperature on the elution of platinum with 1 % NaCN pre-treatment. (0.6% NaOH, 650g/t of Pt)

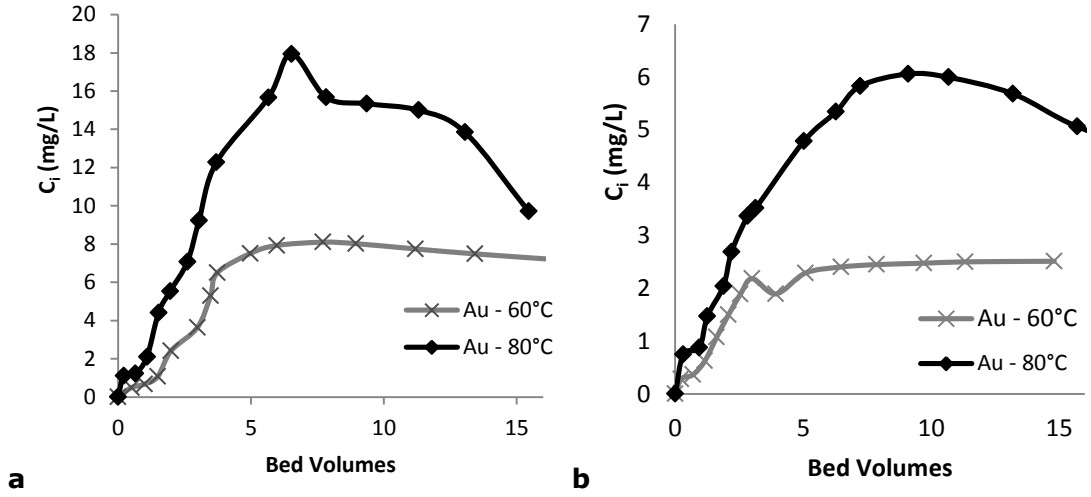


Figure 4.51: The effect of temperature on the elution of gold with a) 2 % and b) 1 % NaCN pre-treatment. (0.6% NaOH, 650g/t of Au)

When the recovery curve is reviewed as shown in Figure 4.52, at 4 bed volumes, a drop in recovery from 99 % for platinum and palladium to 90 and 92 % and then to approximately 64 % and 68 % for Pt and Pd is seen when the elution temperature drops from 95° C to 80°C and then to 60°C. At 5 bed volumes, approximately 99.5% of the Pt and Pd are eluted at 95°C compared with 95% at 80°C and 78% for Pd and 75% for Pt at 60°C. Even though considerably lower, the elution at 60°C for Pt and Pd is still substantial. This is important to note when considering that the high temperature cyanide heap leach and subsequent adsorption are likely to be operated between 50 and 60°C or even higher when tank or autoclave leaching is considered. The negative effect of higher temperatures has also already been discussed in section 4.1.2.1 of this thesis. Van Deventer et al. (1994) stated that the adsorption of gold onto activated carbon is an exothermic process and an increase in temperature will therefore shift the equilibrium to favour elution or desorption.

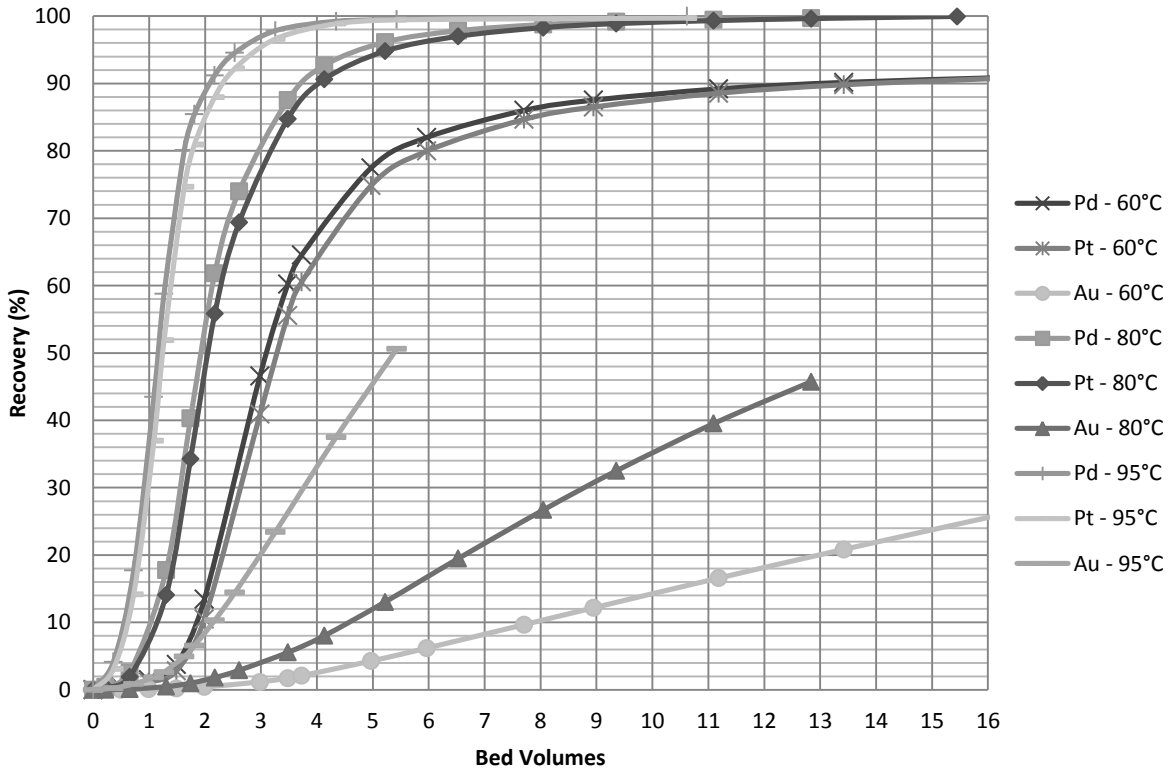


Figure 4.52: PGM elution recovery curve at 60, 80 and 95°C with 2 % NaCN and 0.6 % NaOH pre-treatment.

Stainless steel column elution

The results obtained from the stainless steel column were significantly lower than expected and the recoveries at 4 BVs in comparison to results from the glass elution experiments are shown in Figure 4.53. The lower recoveries were found to be due to the higher flow rates of 30 BV/h for the steel column compared to between 2 and 3 BV/h for the glass column. The conclusion was drawn based on elution experiments carried out at a flow rate of 30 BV/h in the glass column at 80°C and the recovery compared to the recoveries from elution experiments performed at between 2 and 3 BV/h. The higher flow rate elution resulted in a recovery of only 40% compared to 90% at the lower flow rate. The recovery curves can be seen in Figure A.119 in Appendix A.

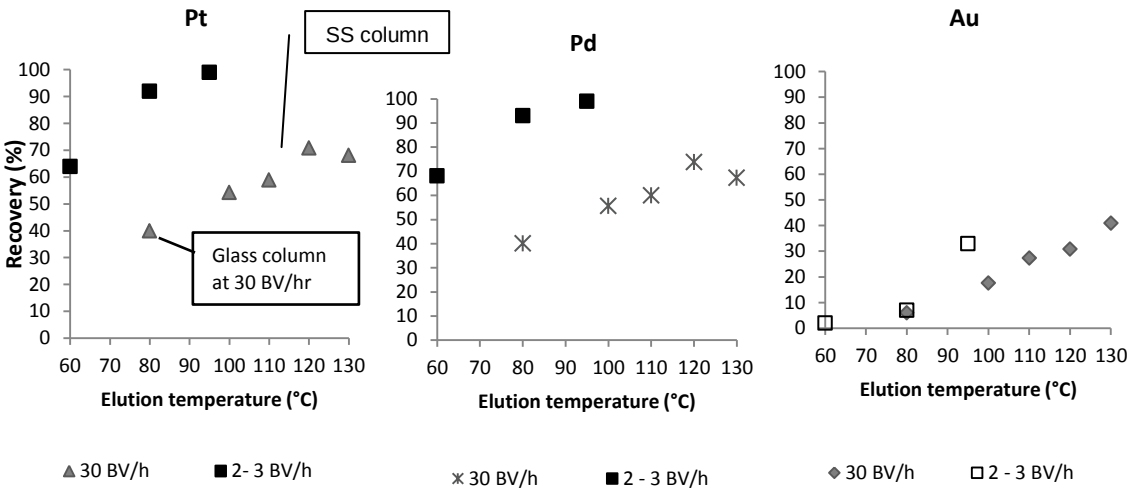
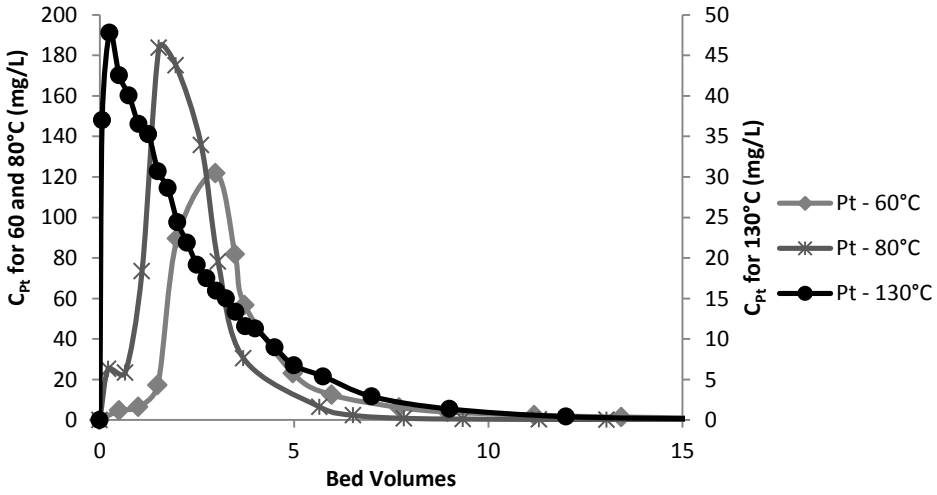


Figure 4.53: The effect of temperature on the elution recovery at 4 BVs in the glass (≈2 BV/hr and one experiment at 30 BV/hr as indicated) and stainless steel columns (30 BV/hr) (Pre-treatment of 2% NaCN and 0.55% NaOH)[*†]

The lower recoveries are therefore not attributed to a breakdown in metal cyanide complexes primarily due to the rising recovery from 100°C to 130°C, which would not have been the case if the metal cyanide complexes did break down with temperature. The gold recovery obtained is also low compared to industry standards for the same range of temperatures. There is, however, some indication of a plateau in the recovery of Pt and Pd, that is reached at 120°C and corresponds to findings by Lunga (2006), who also indicated a plateau in gold recovery at 130°C.

Although a lower recovery was achieved in the steel elution column, comparison of the elution profiles (Figure 4.54) still indicates a shift in the peak towards the left as the temperature increases from 60°C to 130°C.



[*] Novel contribution - Cornelius A Snyders, Steven M Bradshaw, Guven Akdogan, Cleophace N Mpinga, Andries P Van Wyk, Jacques J Eksteen, 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. IMPC, Santiago, Chile, 20 -24 October 2014.

[†] Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

Figure 4.54: Comparison of the elution profiles at 60, 80 and 130°C (Pre-treatment of 2% NaCN and 0.55% NaOH, Carbon loading for 60 and 80°C – 650mg/kg, Carbon loading for 130°C – 300mg/kg)

4.2.1.2 Pre-treatment temperature*

Initial experimentation indicated a rise in recovery of gold as the temperature of the pre-treatment step was increased (Figure A.137 in Appendix A). The results for Pt and Pd were, however, inconclusive.

The effect of the pre-treatment temperature was therefore investigated under more stringent conditions. The recovery profiles (when only considering the PGMs that remained on the activated carbon after pre-treatement and not incorporating the PGMs, that reported to the pre-treatment (PT) solution) for the elutions at the low (25°C) and high (80°C) temperature pre-treatments, were found to be almost identical and are shown in Figure 4.55. The elution profiles at 100°C and 130°C showed a similar result and are shown in Figure A.138 and Figure A.139 in appendix A.

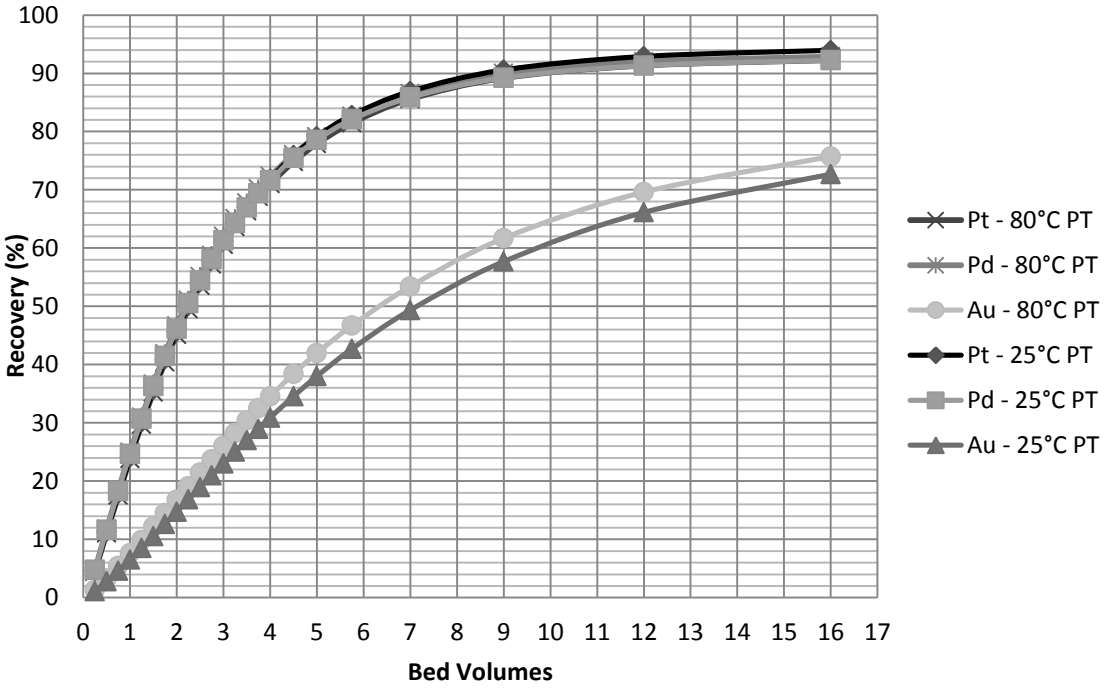


Figure 4.55: Recovery profiles for the elution at 120°C but with pre-treatments (PT) at 25°C and 80°C. (230g/t Pd, 300mg/kg Pt, 500mg/kg Au loadings after pre-treatment with 2% NaCN and 0.55% NaOH)

The amount of PGMs reporting to the pre-treatment solution, however, becomes significant at the higher temperatures and when these PGMs are included in the recovery calculation and considered as a 'loss', the recovery of Pt decreases by approximately 1 to 3%, Pd by 4 to 6%, while gold is almost unaffected as almost no Au is eluted in the pre-treatment step at a pre-treatment temperature of 80°C. (Table A.37 in appendix A) The PGMs reporting to the pre-treatment solution are considered as a 'loss' as a fraction of the PGMs now reports 'elsewhere' instead of the eluate where it is desired. Table 4.28 indicates the recoveries at 4 BVs at a pre-treatment temperature of

* Novel contribution – not published to date

25°C and at 80°C with and without the PGMs to the pre-treatment solution. No PGMs were found to report to the pre-treatment solution at 25°C and are discussed in more detail in section 4.2.3.

Table 4.28: The recovery of PGMs at 4 BVs with pre-treatments at 25°C and 80°C and incorporating the PGMs reporting to the pre-treatment solution at 80°C as a 'loss' (overall recovery).

	Pt			Pd			Au		
	Pre-treatment temperature (°C)			Pre-treatment temperature (°C)			Pre-treatment temperature (°C)		
Elution temperature (°C)	25	80	80 Overall recovery (%)	25	80	80 Overall recovery (%)	25	80	80 Overall recovery (%)
	Elution recovery (%)			Elution recovery (%)			Elution recovery (%)		
100	59	54	53	56	56	52	18	15.5	15.5
110		59	58		60	56	22	21	21
120	72	71	69	72	74	68	31	36	36
130	73	68	66	69	67	62	41	36	36

4.2.1.3 Effect of pre-treatment concentration*†

Apart from being the second most important factor that affects gold elution, the NaCN or $Ca(CN)_2$ in the pre-treatment of the activated carbon is a major operating cost and optimisation of this step is therefore important. Several experiments were completed to determine the effect of NaCN and NaOH in the pre-treatment step on the elution efficiency of Pt and Pd. For convenience, the effect of the NaCN and NaOH concentration is discussed separately in the following sections.

NaCN pre-treatment concentration.

The effect of the NaCN concentration is immediately evident in Figure 4.56 to Figure 4.58 and shows an increase in the recovery of Pt, Pd and Au as the cyanide increases from 0 to 2 % after which the recovery starts decreasing again as the NaCN concentration increases from 2 to 4%. For Au, the effect of NaCN concentration on the recovery is more evident after nine bed volumes than after 4 and is therefore shown here. The NaOH was also found to affect the PGM recovery and at 0% NaCN, an increase in the recovery is seen, while at a higher cyanide concentration (2 and 3% NaCN) a decrease in the PGM recovery occurs when the NaOH concentration is increased from 0.22% to 1.65%. Parabolic equations could be fitted to the experimental data ($R^2 > 0.96$) in order to calculate the cyanide concentration where the maximum recovery occurs, but it is not suggested here that any 2nd order dependence exists. For Pt and Pd, the optimum NaCN concentration was found to be 2.5 % NaCN at 0.6% NaOH, while for Au this value shifted to a slightly higher concentration of 3.4 % at 0.6% NaOH.

* Novel contribution - Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. South African Journal of Mining and Minerals. Vol 113. May 2013. pp 381 – 388.

† Cornelius A Snyders, Steven M Bradshaw, Guven Akdogan, Cleophace N Mpinga, Andries P Van Wyk, Jacques J Eksteen, 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. IMPC, Santiago, Chile, 20 -24 October 2014.

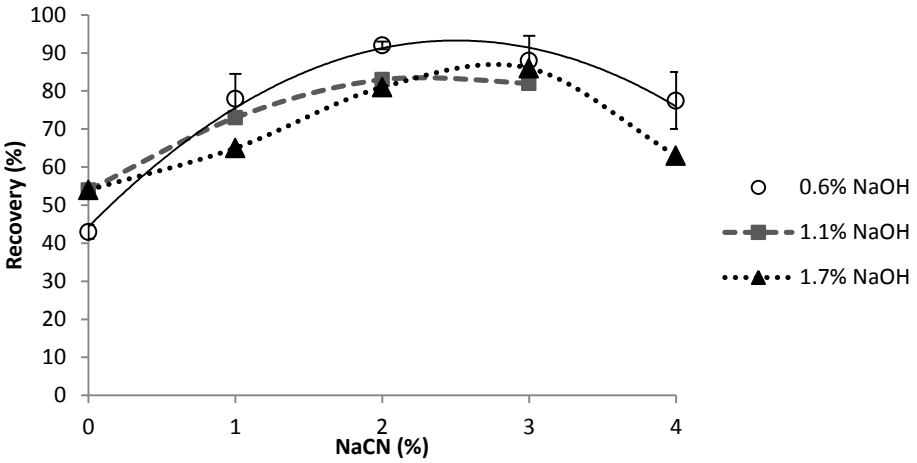


Figure 4.56: Pt recovery after four BV of eluant at varying NaCN and NaOH pre-treatment conditions (Temperature = 80°C, Pt, Pd and Au loading on activated carbon ≈ 650 mg/kg)

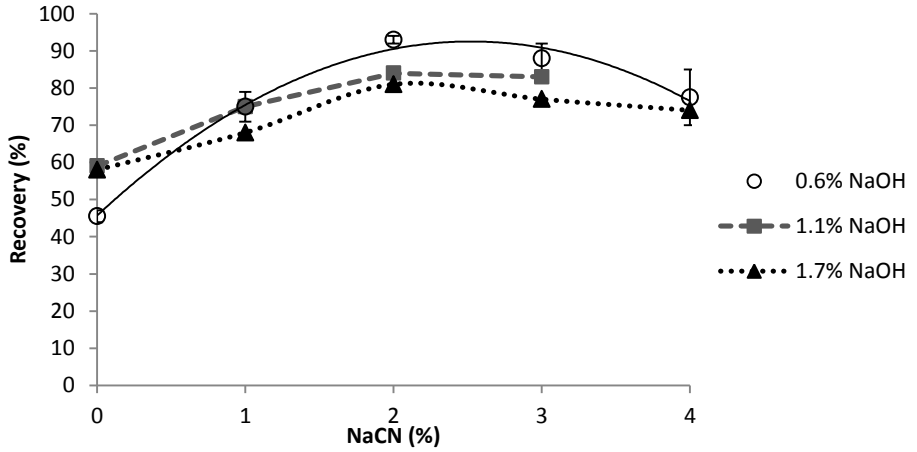


Figure 4.57: Pd recovery after four BV of eluant at varying NaCN and NaOH pre-treatment conditions (Temperature = 80°C, Pt, Pd and Au loading on activated carbon ≈ 650 mg/kg)

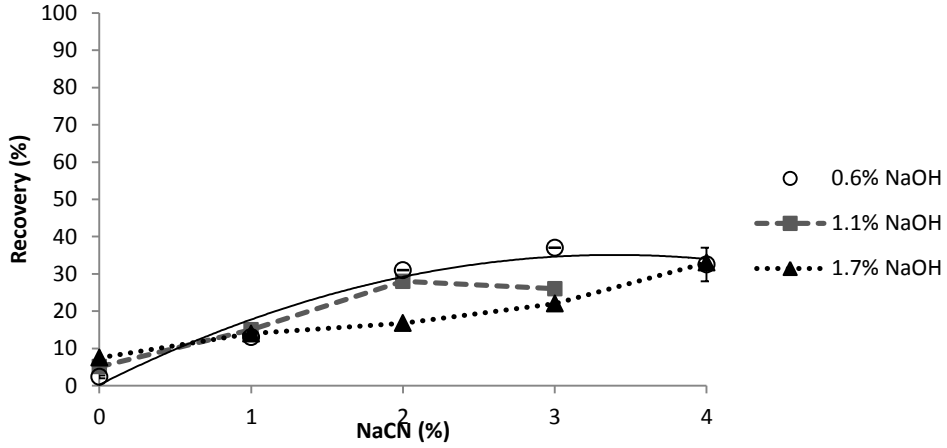


Figure 4.58: Au recovery after nine BV at varying NaCN and NaOH pre-treatment concentrations (Temperature = 80°C, Pt, Pd and Au loading on activated carbon ≈ 650 mg/kg)

Before the increase in Pt and Pd recovery with cyanide concentration is discussed, the well researched gold adsorption and elution are reviewed. The exact mechanism of gold adsorption, and specifically the role of cyanide, remains a discussion point, especially as most authors have substantiated their conclusions adequately by thorough experimentation. The two opposing

theories are whether partial chemical degradation of $NaAu(CN)_2$ to AuCN on the activated carbon surface occurs or not. Authors who suggested partial degradation in the past are McDougall et al. (1980), Tsuida and Muir (1986), Cook et al. (1989) and Cook et al. (1990). The degradation of $NaAu(CN)_2$ would explain the reason why cyanide is required (for conversion back to the form $[Au(CN)_2]^-$ which can be desorbed) to increase the gold elution recovery. Cyanide free elutions performed by Jones et al. 1989, Adams and Fleming, 1989, Boshoff, 1994 contradict the theory of a partial degradation, as do the results of Adams (1991), who studied gold adsorption with Mossbauer spectroscopic investigations and found that the gold present on the activated carbon is solely the $[Au(CN)_2]^-$ ion. Adams (1991) also stated that no commercial activated carbon products are sufficiently powerful reducing agents (E = -0.16 to 0.16 V) to reduce the aurocyanide ion (E^0= -0.79 V) unless under acidic conditions, which Adams found (Adams et al. 1987) can lead to some decomposition of $Au(CN)_2^-$ to Au(CN).

Van Deventer and Van der Merwe (1993) ascribed these different results from different authors to the different samples of activated carbon used. Through elution tests, FTIR scans (Fourier Transform Infrared Scan) and XPS analysis (X-ray Photoelectron scans), they found that carbon from different manufacturers as well as carbon from the same manufacturer with the same specifications, but from different batches, has different tendencies of converting $Au(CN)_2^-$ to AuCN. One batch of activated carbon at a pH of 8.5, room temperature and with no added cyanide converted 21% of the gold to AuCN, while the other batches of carbon did not. The formation of AuCN could also be enhanced by lowering the pH (3.5) and increasing the temperatures (110°C). In reference, activated carbon used for the present study, showed that after adsorption from solutions containing only gold (Figure 4.59) (to eliminate the possible interference of Pt and Pd), no cyanide in the pre-treatment step resulted in low recoveries with only 8% being recovered after 14 BVs compared to 44% after 14 BVs with a 2% NaCN pre-treatment. It is therefore considered to be highly likely that AuCN formed on the activated carbon due to the strong need for NaCN for elution.

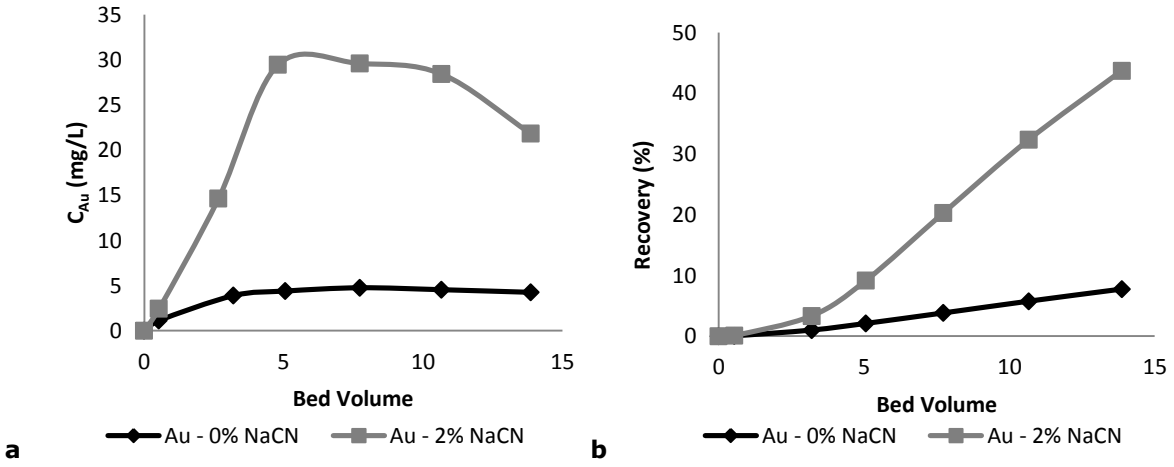


Figure 4.59: The elution profile (a) and recovery (b) of Au only after pre-treatment at 0 and 2% NaCN pre-treatment strengths at 0.55% NaOH at 25°C for the pre-treatment and 80°C for elution.

From Figure 4.59, it can, however, be argued that it is merely in a change in elution kinetics and not complete proof of the formation of AuCN as Figure 4.59 still shows ongoing elution after 14 BVs. A mere change in elution kinetics was therefore considered first for Pt and Pd elution by evaluating the elution profiles at various cyanide pre-treatment concentrations, which are shown in

Figure 4.60 and Figure 4.61. For Pt and Pd, both figures show that the bulk of the elution occurs within the first 5 BVs. After 15 BVs, the elution essentially stops with only trace elements (≤ 1 mg/L) of Pt and Pd still found in the eluant.

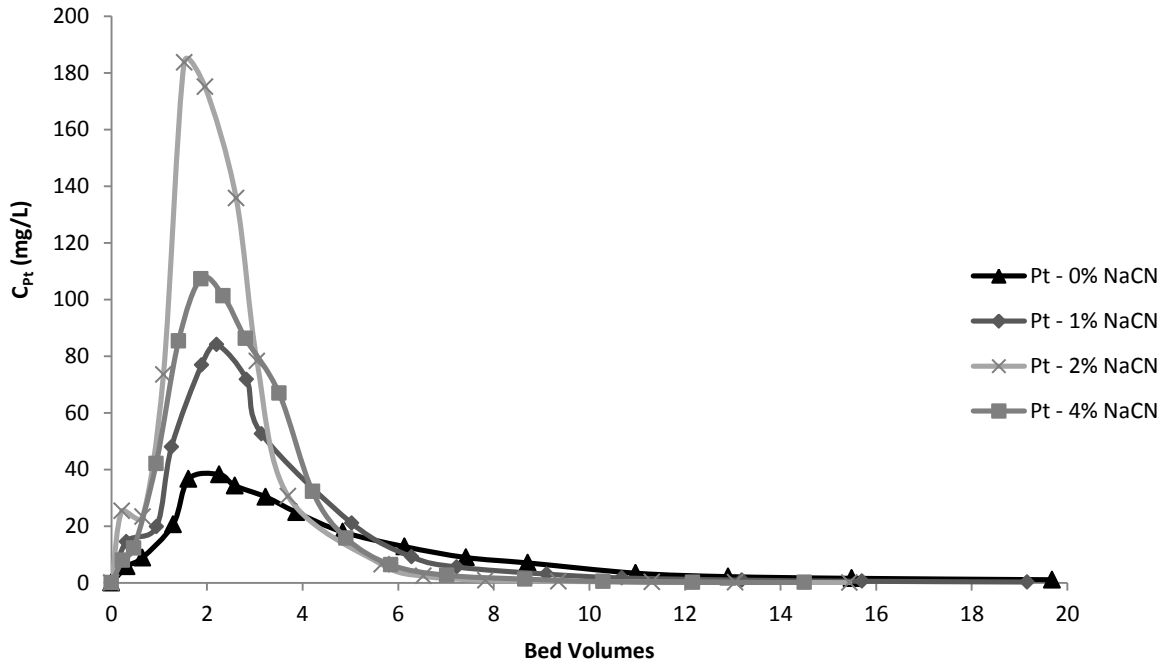


Figure 4.60: The effect of cyanide pre-treatment on the elution of platinum cyanide at 0.55% NaOH pre-treatment and 80°C

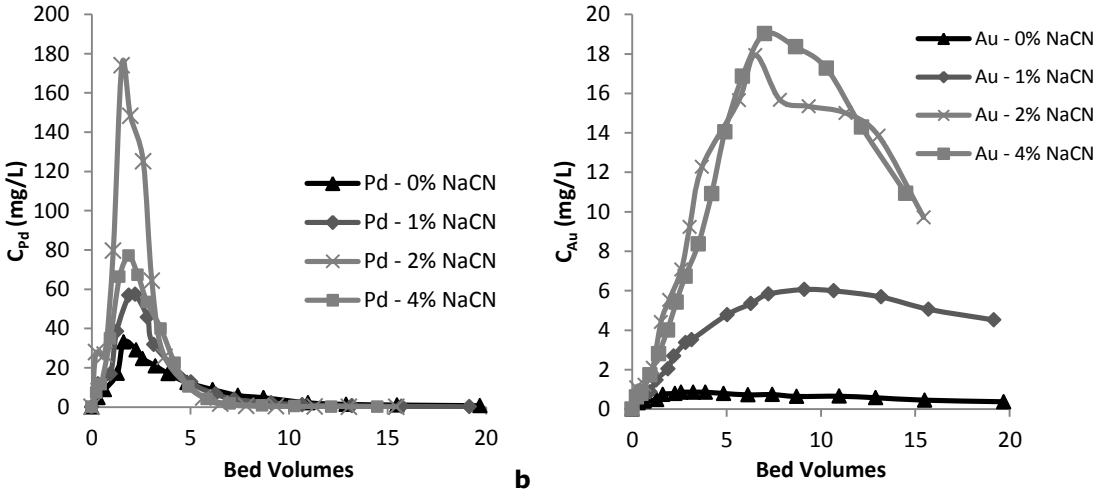


Figure 4.61: The effect of cyanide pre-treatment on the elution of a) palladium- and b) gold cyanide at 0.55% NaOH pre-treatment and 80°C

The likelihood of more than one cyanide complex for Pt and Pd with different adsorption characteristics was therefore researched secondly. PGM adsorption studies by Vorob'ev-Desyatovskii et al. (2012) revealed at least two platinum compounds and two palladium compounds on the activated carbon surface. The majority (> 90%) of these complexes were the tetracyanopalladate(II) ($[Pd(CN)_4]^{2-}$) and the tetracyanoplatinate(II) complex ($[Pt(CN)_4]^{2-}$). The second compounds were speculated to be $[Pd(CN)_2]$ and $[Pt_2(CN)_{10}]^{4-}$.

Monlien et al. (2002) suggested that for Pt and Pd, that pentacoordinated species do occur (reaction 4.3) while Sharpe (1976) proposed Eq. 4.3 for Pd. It was therefore concluded here, that the occurrence of more than one platinum or palladium cyanide complex on the activated carbon surface, is likely, but probably only to a fairly small degree, when considering the high stability constants (log β) of 40 for $[Pt(CN)_4]^{2-}$ and 51.7 for $[Pd(CN)_4]^{2-}$.

$$[Pd(CN)_4]^{2-} + CN^- \leftrightarrow [Pd(CN)_5]^{3-} \quad (4.3)$$

The formation of $Pd(CN)_{2(s)}$ on the activated carbon surface was also considered. This precipitate is insoluble in water and will require cyanide (Eq. 2.13) to re-dissolve the precipitate. This proposed reaction for palladium is similar to what Fisher and LaBrooy (1997) found for Ni adsorption and elution when an acid pre-treatment step is involved. Acid washing of carbon loaded with nickel results in the formation of a $Ni(CN)_{2(s)}$ precipitate from $Ni(CN)_4^{2-}$, which requires a cyanide pre-treatment step for effective elution. As with Ni, the formation of small (not quantified) quantities of $Pd(CN)_{2(s)}$ was found (Hancock and Evers, 1976) to occur under acidic conditions (2 M HCl and after a few days) but since adsorption mainly took place at alkaline conditions (pH = 9.5) in this case, this reaction was deemed to be an unlikely explanation for the requirement of cyanide for effective Pd elution. Hibble et al. (2011) also showed that solid $Pt(CN)_2 \cdot 0.76H_2O$ could be prepared through a solution of $K_2Pt(CN)_4$ and $K_2Pt(Cl)_4$.

An alternative explanation is that the presence of cyanide, and to a lesser extent NaOH, causes a change in the functional groups on the carbon surface, which makes the surface less receptive to adsorption (Van der Merwe and Van Deventer, 1990, Adams 1991).

Analysis of the specific cyanide complex on the activated carbon poses certain challenges. The difficulty with the analysis is both the concentration of the absorbed species and a large scattering response from the carbon which swamp the minor species. Both FTIR and Raman spectroscopy were used to analyse for the adsorbed Pt and Pd complexes on the activated but no conclusions could be drawn from the results. Since the exact complexes of Pt and Pd cyanide occurring on the activated carbon surface could not be confirmed through measurement, it is therefore difficult to come to a definite conclusion as to which of the above mentioned theories are more relevant to explain the increase in the elution kinetics and recovery of Pt and Pd with an increase in cyanide pre-treatment.

The decrease in the elution rate of gold at higher cyanide concentrations is ascribed to the increasing ionic strength or the increase in ions such as Na^+ (Adams, 1991 and Davidson and Bailey, 1991). For Pt and Pd specifically, an increase in the ionic strength also resulted in a decrease in the elution recovery (as per section 4.2.1.4) and therefore concluded to be the main cause for the decrease in elution recovery as the cyanide concentration increased.

Cyanide treatment at a lower elution temperature

At the lower temperature of 60°C, a decrease in PGM elution efficiency can again be seen when the cyanide concentration in the pre-treatment step is decreased and is consistent with the above mentioned findings (Figure 4.62).

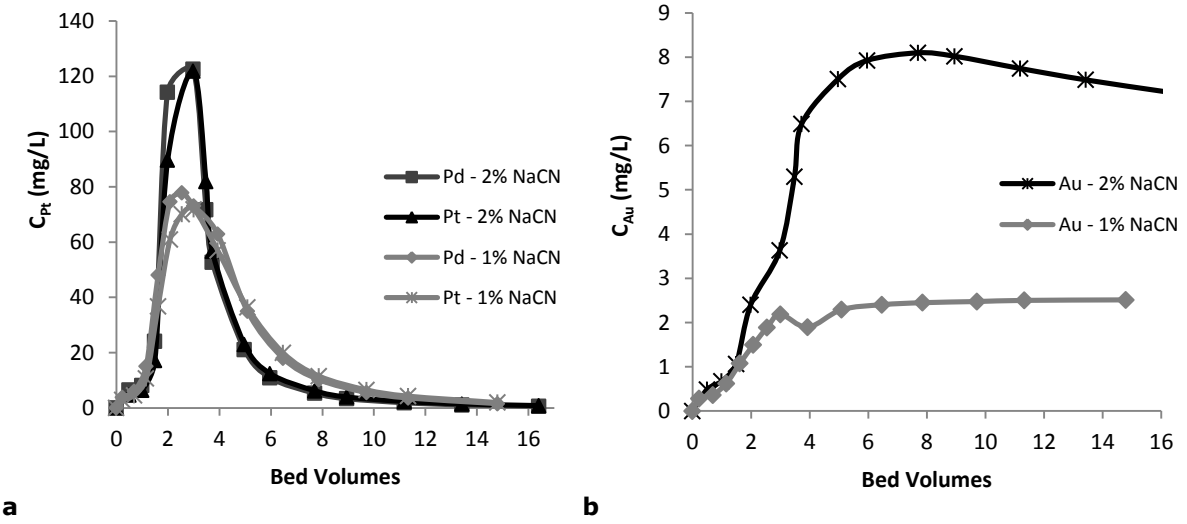


Figure 4.62: The effect of cyanide pre-treatment on the elution of a) platinum and palladium- and b) gold cyanide at 0.55% NaOH pre-treatment and 60°C

NaOH pre-treatment concentration.*

Following on from Figure 4.56 to Figure 4.58 the effect of NaOH is shown in the presence of no cyanide (Figure 4.63a) and 2% cyanide (Figure 4.63b).

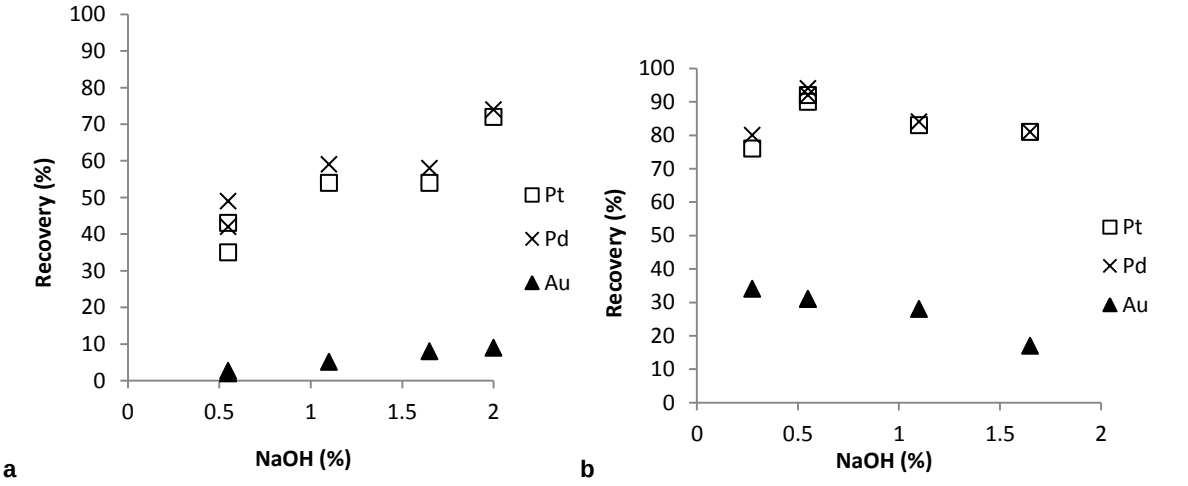


Figure 4.63: Elution recovery of Pt, Pd after four BV and Au after nine BV at varying NaOH pre-treatment concentrations at a.) 0% NaCN and b.) 2% NaCN at 25°C for the pre-treatment and 80°C for elution.

From Figure 4.63a an increase in the elution recovery for Pt, Pd and Au is seen as the NaOH concentration is increased. Fleming and Nicol (1984) and McDougal et al. (1980) observed that the equilibrium loading of gold cyanide is enhanced by lowering the pH. A higher pH will therefore favour the desorption process and explains the increase in the elution recovery in Figure 4.63a as well as the increase for Pt and Pd seen in Figure 4.63b as the NaOH increases from 0.25% to 0.55%. As with the addition of NaCN, an optimum addition of NaOH was also found at 0.55%, but the effect thereof (NaOH) on the elution of the PGMs was much less pronounced

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

Figure 4.63a and b is supported by the results found by Davidson and Duncanson (1977), which showed an increase in the elution recovery of nickel as the NaOH concentration in the pre-treatment increased from 0 to 1%. As the NaOH concentration, however, increased from 1 to 20%, the elution recovery for gold, silver and nickel decreased, which Davidson and Duncanson (1977) related to the stability of the silver, copper and nickel cyanide complexes being lower at high pH values. The decrease in the Pt, Pd and Au recoveries are, however, rather attributed to the increase in the ionic strength, rather than the stability of the complexes due to the much higher stability constants of Pt, Pd and Au compared to Ag, Cu and Ni as per Table 2.2 in section 2.6.

4.2.1.4 Effect of the ionic strength*

The third most influential factor, according to Adams and Nicol (1986) is the ionic strength of the eluant, and according to literature, an increase in ionic strength will result in a decrease in elution efficiency. Mcdougal (1980) and Van Deventer and Van der Merwe (1994) reported the beneficial effect of the cations on the adsorption of Au to be in the order $Ca^{2+} > Mg^{2+} > H^{+} > Na^{+} > K^{+}$ and the negative effect on the elution is therefore expected to follow the same sequence.

The effect of increasing ionic strength of the elution water, represented here by an increase in Na^{+} cations on the elution recovery of Pt and Pd, is shown in Table 4.29. As expected, a decrease in Pt, Pd and Au recovery is seen as the ionic strength of the elution water increases.

Table 4.29: Elution recovery of Pt, Pd and Au with increasing eluant ionic strength after a pre-treatment with a 2% NaCN and 0.55% NaOH solution at 80°C (Pt, Pd and Au loading on activated carbon ≈ 650 mg/kg)

Eluant		Recovery (%)		
Na^{+} (mg/L)	BV	Au	Pd	Pt
0	5	12	95	94
80	5.5	5.0	90	87
154	5.0	4.7	87	85
187	5.3	4.1	88	86
301	5.1	3.6	82	79

4.2.1.5 Effect of PGM concentration/Carbon Loading†

Figure 4.64 shows the elution curve from the high loaded activated carbon compared to the elution of lower loaded activated carbon. The initial rate of elution ($\frac{dQ_{i,t}}{dt}$) from the high loaded activated carbon is faster as indicated by the higher slope on the curve. The elution then slows down with peak around 2.5 bed volumes. The elution concentration then decreases rapidly, but with a substantial amount of PGMs (400 mg/kg Pt and 320 mg/kg Pd) still left on the AC at 4 bed volumes compared to little (20 mg/kg Pt and Pd) with the lower loaded AC. From 5 bed volumes onwards, the rate of elution then decreases substantially with 10 and 6 mg/kg Pt and Pd respectively still left

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

† Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

at 12 bed volumes. The elution recovery as indicated by Figure 4.64b shows a shift in recovery towards the right indicating slower recovery ($\frac{dQ_{i,t}/dQ_{i,o}}{dt}$) with the higher loaded activated carbon.

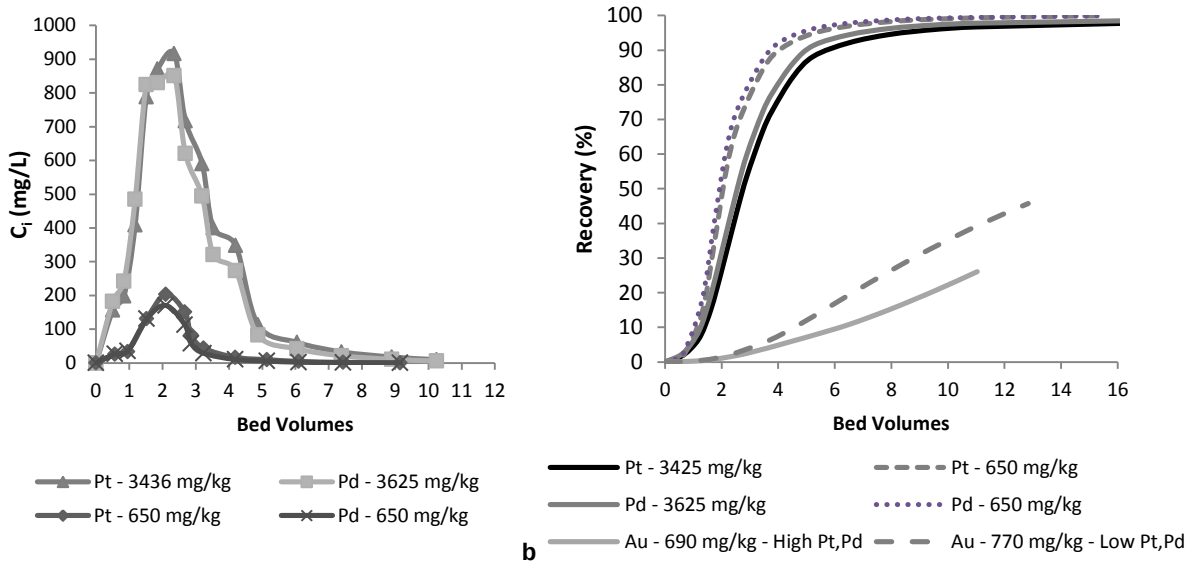


Figure 4.64: The elution of platinum, palladium and gold at low (650 mg/kg of Pt, Pd and 770 mg/kg Au) and high (3436 mg/kg Pt, 3625 mg/kg Pd and 690 mg/kg Au) carbon loading after pre-treatment with a caustic cyanide solution (2% NaCN, 0.55% NaOH) at an elution temperature of 80°C.

These results are opposite to what Boshoff (1994), Van der Merwe (1991) and Davidson and Duncanson (1977) suggest, but correspond to observations by Van Deventer and Liebenberg, (2003) who found a decrease in the elution recovery as the loading on the activated carbon increased. Pleysier et al. (2008) and Vegter (1992) indicated that, although gold adsorption predominantly occurs on the external surface of the activated carbon, once the external surface becomes saturated slower transport into the interior of the activated carbon occurs. Van der Merwe (1991) stated the higher the initial concentration and the shorter the adsorption time, the more gold will be adsorbed closer to the particle surface and showed through subsequent experimentation that the elution rate was higher for carbons, which had steeper gold concentrations gradients (carbon that was loaded with gold over shorter periods of time). Longer adsorption times will lead to more gold diffusing into the carbon. Considering Figure 4.64 , the elution profile from a batch of activated carbon loaded to approximately 650 mg/kg Pt and Pd each, which was adsorbed over a period of 65 hours, is compared to an elution profile from a batch that was loaded to equilibrium over a period of 120 hours. It is therefore most likely that the carbon, that was loaded for longer and until equilibrium was reached, had more PGMs diffused into the carbon, which led to slower elution kinetics. One of the arguments put forward by Van Deventer and Liebenberg (2003) is that with an increase in the gold loading, the elution process shifts from equilibrium to mass transfer controlled, which leads to slower elution kinetics.

This change in the elution recovery kinetics ($\frac{dQ_{i,t}/dQ_{i,o}}{dt}$) of Pt and Pd with the carbon loading is therefore explained by the proximity of the loading on the activated carbon to its surface saturated values. With surface saturation reached, the PGMs will start diffusing into the activated carbon

particle, which occurs at a slower rate and will therefore desorb at a slower rate as well resulting in a lower recovery at a similar BV for high metal loadings.

It is therefore hypothesized that at relatively low carbon metals loadings and short adsorption times, an increase in the metal loading will result in improved or at least similar elution recoveries as found by Van der Merwe (1991). As the carbon surface becomes saturated with metal and diffusion into the macro and micro pores occurs, the elution will become slower and less efficient at similar bed volumes than with lower loaded activated carbons. It is therefore suggested here, that a carbon loading level may exist, which will lead to optimum elution recoveries.

From the recovery curve in Figure 4.64b, it is also interesting to note the decrease in the gold recovery. The reason here is attributed to one or possibly both of the following two options:

1. The increase in the gold recovery is due to the higher loading, but which did not reach an equilibrium stage and which corresponds to the findings by Boshoff (1994), Van der Merwe (1991) and Davidson and Duncanson (1977).
2. The slower elution of the lower Au loaded activated carbon (690 mg/kg) is due to the presence of significantly higher loadings of Pt and Pd, which are diffused into the macro and micro pores of the activated carbon and shown to elute with slower kinetics. The higher Au loaded carbon (770 mg/kg) contained the lower loadings of Pt and Pd. Considering the order of PGM adsorption, as found by Mpinga (2012) (which is also supported by this investigation as discussed in section 2.4.4) is:

$$[Au(CN)_2]^- > [Pt(CN)_4]^{2-} > [Pd(CN)_4]^{2-} > [Ni(CN)_4]^{2-} > [Cu(CN)_3]^{2-}$$

gold is adsorbed first and is therefore likely to get trapped and the elution thereof reduced when slow or slower elution of Pt and Pd occurs. This occurs in a similar fashion as when gold elution is reduced when copper loadings are high and the cyanide in the pre-treatment step is low (Boshoff, 1994, Van Deventer and Liebenberg, 2003).

To verify the above mentioned theory, the adsorption preference (based on SEM-EDX analysis as per section 4.1.1) of Pt was broadly determined by dividing the activated carbon outer area into three sections namely:

1. Surface – area between pores
2. Near pores – edge of carbon pores
3. Pores – inside the activated carbon pores

and comparing the concentrations in these areas for a high Pt loading (16800 mg/kg) and a lower loading (2140 mg/kg). The results of the plot can be seen in Figure 4.65 and show higher concentrations of Pt inside the pores for the high loading, while at the lower loading the distribution is more equal between the three regions.

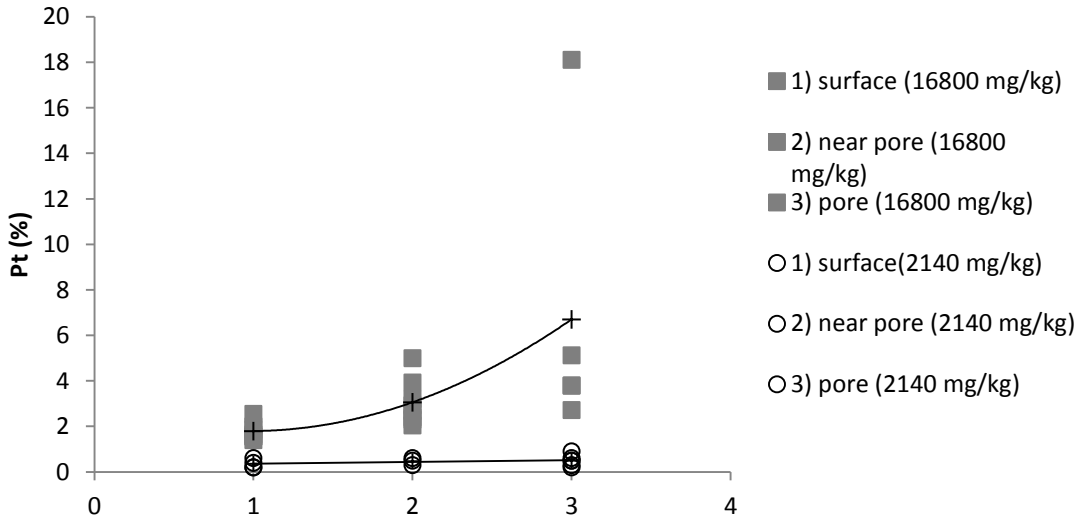


Figure 4.65: Pt adsorption preference as determined by SEM-EDX for a high loaded (16800 mg/kg) and a lower loaded (2140 mg/kg) activated carbon.

An additional set of experiments was also completed to confirm the above mentioned theory and the results can be seen in Figure 4.66. The results from Figure 4.64 are incorporated into Figure 4.66 for more complete representation of the data. The results, as indicated by the SEM-EDX analysis in Figure 4.65 and the experiments shown in Figure 4.66, agree with the hypothesis that at relatively low carbon metal loadings, an increase in the Pt and Pd loading will result in improved recoveries up to a point. At higher loadings (with diffusion into the macro and micro pores), the elution becomes slower and less efficient at similar BVs. Although this theory could not directly be verified, it is expected that the increase in Pt and Pd elution recovery with lower loadings are related to the binding mechanism of these ions to the activated carbon. Vorob'ev-Desyatovskii et al. (2012) stated that the cyanometallate bind to active centres on the activated carbon surface which act like anchors and further anions are then "stacked" through the formation of metallophilic bonds. If the "anchor" is then broken during the elution process, higher stacks of ions will result in a higher elution recovery for the PGM cyanides situated on the surface of the carbon.

A similar conclusion could not be drawn for Au from the data presented here, but rather shows a recovery in a narrow band between 5 and 7% as the Au loading increase from 300 mg/kg to 1150 mg/kg and corresponds to findings by Boshof (1994), who stated that the elution inefficiency is rather insensitive to the gold loading. Since the capacity of activated carbon is higher for gold than for Pt and Pd, it is recommended that higher loadings of gold is investigated at conditions more appropriate to gold elution (120 -130°C) to obtain a more clear understanding of the effect of gold loading on the elution efficiency.

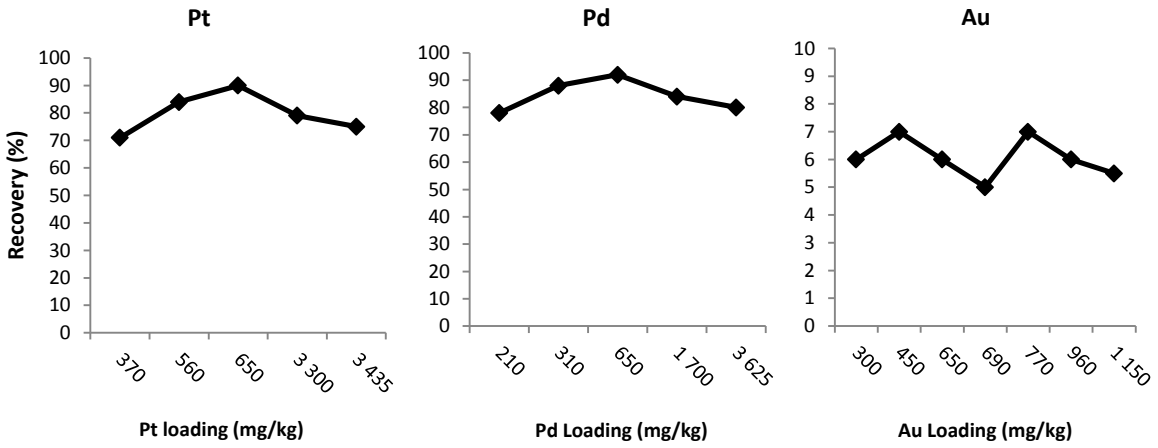


Figure 4.66: The effect of carbon loading on PGM recovery at 4 BVs (pre-treatment with 2% NaCN and 0.6% NaOH at an elution temperature of 80°C) (Horizontal axis not to scale)

4.2.1.6 Effect of Copper*

Figure 4.67 shows the elution of the PGMs in the presence of copper cyanide complexes. Copper cyanide elutes first and almost to completion within the first two bed volumes followed by simultaneous elution of palladium and platinum and with gold eluting last.

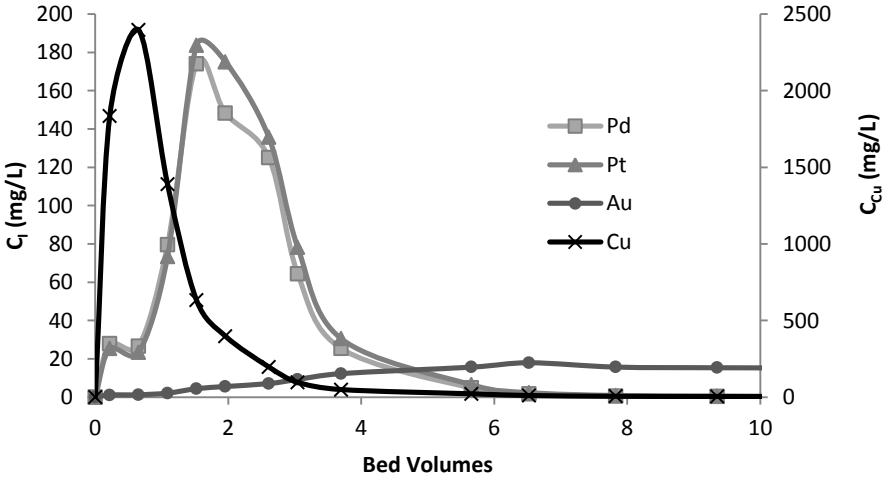


Figure 4.67: The elution of Cu, Pt, Pd and Au from loaded activated carbon (650g/t of Pt, Pd and Au each, 5360g/t Cu) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.6% NaOH) with an elution temperature of 80°C

The cyanide pre-treatment has also been found to have a major influence on the elution of Cu (Figure 4.68) and can be explained by the formation of the different copper complexes, as discussed in section 2.5.6.1, which have different tendencies to absorb. The more free cyanide present, the greater the tendency of $[Cu(CN)_4]^{3-}$ complexes forming, which don't adsorb and which will therefore easily elute. The associated PGM elution profiles (for Figure 4.68) are shown in Figure A.120 and Figure A.121 in Appendix A.

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

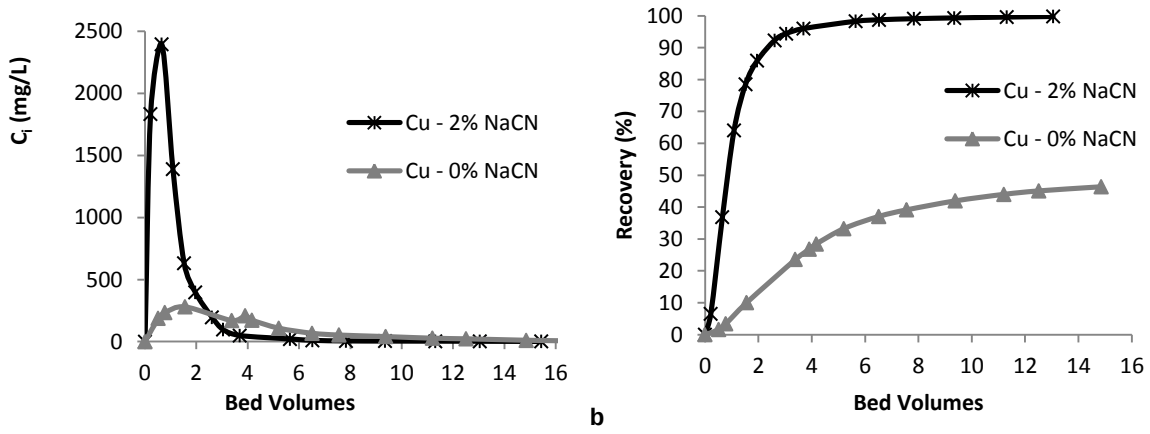


Figure 4.68: Comparison of Cu elution with and without cyanide pre-treatment. (Carbon loading - 650g/t of Pt, Pd and Au each, 5360g/t Cu, elution temperature of 80°C)

Similar to the findings by Boshoff (1994) and Van Deventer and Liebenberg (2003), the presence of Cu did not have a negative effect on the elution of Pt, Pd or Au at strong pre-treatment conditions as similar recovery curves with and without Cu were found (Figure 4.69) In this case, the effect of the corresponding Na^+ during the elution runs is also considered. Van Deventer (1990) found that Au elution only occurs when the bulk of the Na^+ cations have been removed and if an elution run has a high amount of Na^+, which takes longer to be removed from the column, it will have a reducing effect on the PGM recovery. The amount of Na^+ in the PGM elution without Cu is therefore evaluated to ensure that it was not sufficiently high, that it could have forced the PGM elution recovery curve to the right, where it would have coincided with the PGM recovery curve that did contain Cu ultimately hiding the reducing effect of the Cu. Since the elution without copper has less Na as per Figure 4.69b, it is does not result in a lower recovery curve and the conclusion that the Cu does not have a reducing effect on the PGM recovery at strong pre-treatment conditions remains valid.

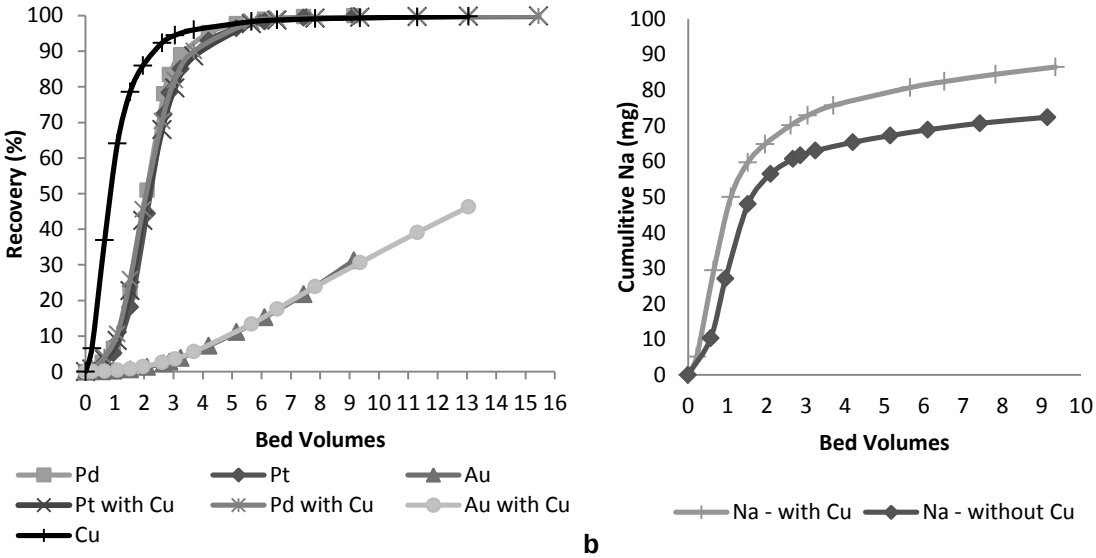


Figure 4.69: a) The elution recovery of PGMs and Cu and b) the corresponding Na elution indicating more Na+ were present during the elution run, which included copper (650g/t of Pt, Pd and Au each, 5360g/t Cu after pre-treatment with 2% NaCN and 0.55% NaOH at 80°C.

At weak pre-treatment conditions (< 2 % cyanide concentration), Van Deventer and Liebenberg (2003) argued that copper has arguably the most detrimental effect on the elution of gold. Figure 4.70 shows the effect of copper after pre-treatment with 0.55% NaOH and no cyanide. The recoveries of Pt and Pd from solutions, which did contain Cu (22% Pt and 32% Pd at 4 BVs), are substantially lower than the experiments, which did not contain copper (35 and 43% Pt, 42 and 40% Pd at 4 BVs) and therefore correspond to the findings by Van Deventer and Liebenberg (2003) and Boshoff (1994). However, considering the corresponding Na^+ elution profiles (Figure 4.71) for the three recoveries curves it can be seen that Experiment O, which shows the highest recovery, corresponds to the lowest amount of Na^+ and the Pt and Pd recoveries where Cu was present, have the highest amount of $Na^{+,}$ which took the longest to elute from the column. It can thus be argued that it is the higher Na^+ ions, that forced the Pt and Pd with Cu curves to the right and not the Cu itself. The effect of Na^+ cations were investigated through modelling and the effects discussed in section 5.7.

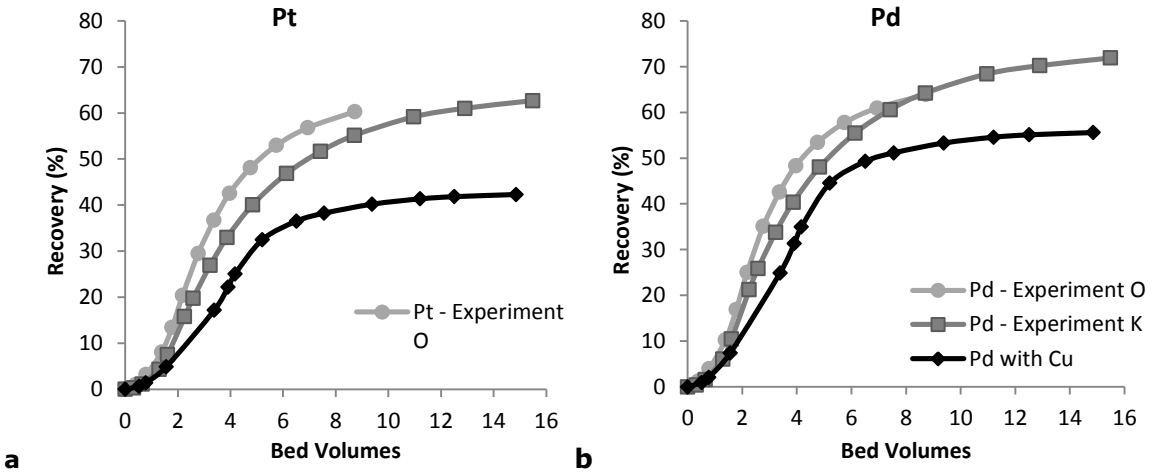


Figure 4.70: The elution recovery of Pt and Pd with and without Cu (Experiment O and K: 650g/t of Pt, Pd and Au each with no Cu with Experiment K having slightly more Na; Elution for experiment with Cu: 650g/t of Pt, Pd and Au each, 5360g/t Cu) (pre-treatment with 0% NaCN and 0.55% NaOH at 80°C.)

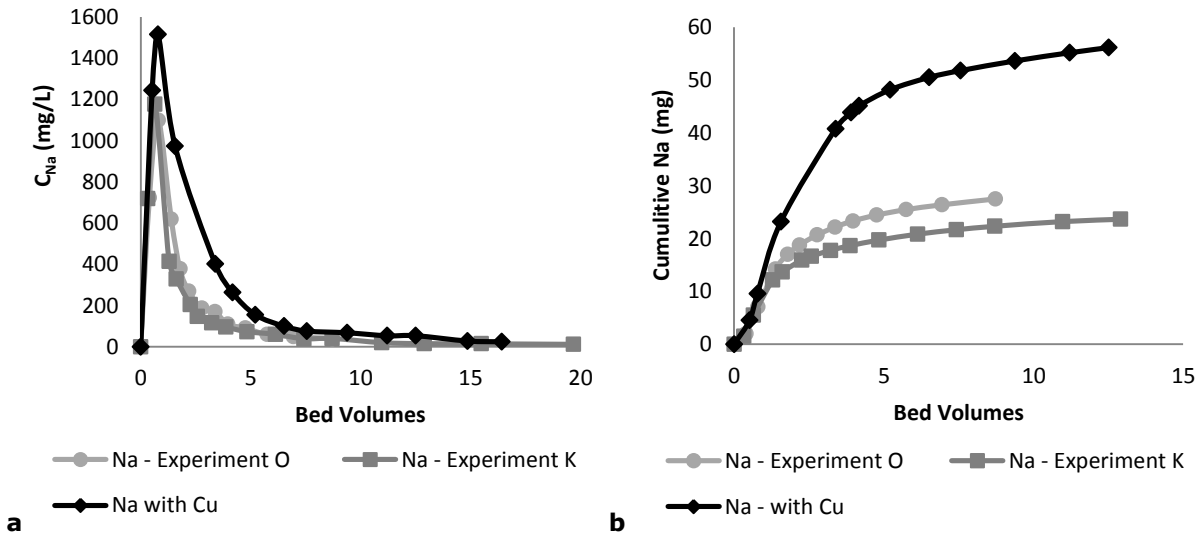


Figure 4.71: The corresponding Na elution profile indicating more Na+ was present during the elution run, which included copper (650g/t of Pt, Pd and Au each, 5360g/t Cu after pre-treatment with 0% NaCN and 0.55% NaOH at 80°C.)

4.2.1.7 Effect of Thiocyanate (KSCN)*†

As South African PGM bearing ores are often associated with large amounts of sulphides (Cramer, 2001) a high concentration of SCN^- is expected to be present in leach solution due to the reaction of sulphur and cyanide. The effect thereof on the adsorption on Pt and Pd has been investigated (Mpinga, 2012) with no substantial negative influence found. For the elution, however, it has been found that the presence of 100 mg/L KSCN salt added to the leach solution during the adsorption stage, reduces the elution recovery of the PGMs at 5 bed volumes from 95% for Pt and Pd, when not present to approximately 78% when present (Figure 4.72). The corresponding Na^+ elution was evaluated again and found to be in a very similar range for both of the experiments and shown Figure A.127 in Appendix A.

A possible explanation may be due to the additional K^+ ions and not necessarily due to the presence of SCN^- and remains to be tested. An alternative explanation is that the Pt and Pd form a bond with thiocyanate ($[Pt(SCN)_4]^{2-}$ and $[Pd(SCN)_4]^{2-,}$ as per Hamáček and Havel, 1999), which adsorb onto carbon, but don't desorb with water. Stability constants, however, for $[Pt(SCN)_4]^{2-}$ is given as 33.6 and $[Pd(SCN)_4]^{2-}$ as approximately 25 (Bahta et al. 1997) and therefore less stable than the respective cyanide complexes.

The elution profiles for Au and Cu in the presence of KSCN were evaluated as well and found to be reduced by the presence of KSCN in a similar manner to that of the Pt and Pd. The elution profiles are shown in Figure A.125 and Figure A.126 in Appendix A.

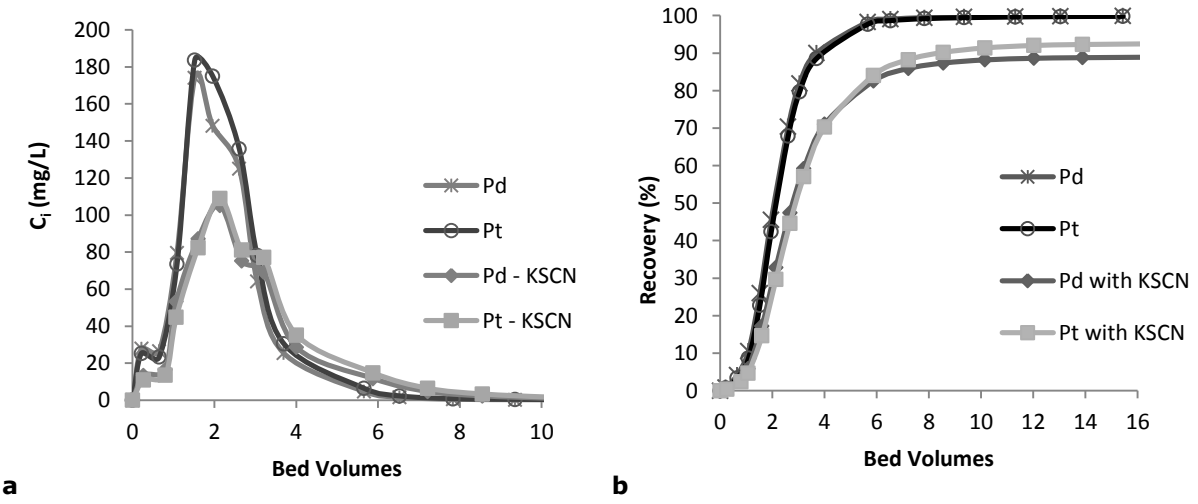


Figure 4.72: The elution recovery of Pt and Pd in the presence of KSCN salt (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH and elution at 80°C.)

* Novel contribution - Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. South African Journal of Mining and Minerals. Vol 113. May 2013. pp 381 – 388.

† Cornelius A Snyders, Steven M Bradshaw, Guven Akdogan, Cleophace N Mpinga, Andries P Van Wyk, Jacques J Eksteen, 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. IMPC, Santiago, Chile, 20 -24 October 2014

4.2.2 Acid treatment*

The effect of hydrochloric acid treatment on the elution of Pt and Pd can be seen in Table 4.30. For all the cases, the Pt and Pd recovery increased when acid pre-treatment was performed. In none of the cases did any of the Pt, Pd or Au elute with the acid or the following rinsing water at 25°C.

As found previously (Grimsley, 1991, Van der Merwe, 1991, Davidson and Baily, 1991), no copper was eluted with cold acid, although up to 3% Cu was eluted with hot acid. No Ni was eluted with the cold acid, but a significant 64 to 75% with the hot acid pre-treatment. Following the hot acid pre-treatment an additional 9.1 to 10.5 % Ni was eluted with the rinsing water. It is also interesting to note the lowest recovery of copper occurs when the acid concentration is high (3M) and hot (70°C). This is hypothesized to be due to the increased formation of either CuCN or $[Cu(CN)_2]^{-}$, which requires a more concentrated or simply a longer cyanide pre-treatment step to convert the copper cyanide complexes to $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, which readily elutes with hot de-ionized water (Boshoff, 1994, Adams, 1991, and Lu et al. 2002).

Table 4.30: The effect of hydrochloric acid pre-treatment on the elution recoveries of Pt, Pd and Au as well as Cu and Ni followed by a pre-treatment with a 2% NaCN and 0.55% NaOH solution at an elution temperature of 80°C (Carbon loadings: Pt – 320 mg/kg, Pd – 253 mg/kg, Au – 526 mg/kg, Cu – 366 mg/kg, Ni – 3580mg/kg (Appendix B))

		Recovery (%)					
		BV	Au	Pd	Pt	Cu	Ni
NONE	Eluant (water - 80°C)	5.2	4.1	76.8	71.5	83.8	81.4
	ACID 1	3.1	0.0	0.0	0.0	0.1	0.1
1 M COLD HCl (25°C)	Rinse water 1 (25°C)	7.7	0.0	0.0	0.0	0.1	0.0
	Eluant 1 (water - 80°C)	5.2	6.9	79.0	74.8	85.9	79.8
	ACID 2	3.1	0.0	0.0	0.0	0.0	0.3
3 M COLD HCl (25°C)	Rinse water 2 (25°C)	7.7	0.0	0.0	0.0	0.0	0.1
	Eluant 2 (water - 80°C)	5.2	4.8	89.2	83.9	83.5	81.4
	ACID 3	3.1	0.0	0.0	0.0	1.3	63.7
1 M HOT HCl (70°C)	Rinse water 3 (25°C)	7.7	0.0	0.0	0.0	0.2	10.5
	Eluant 3 (water - 80°C)	5.2	12.3	92.1	88.6	95.4	24
	ACID 4	3.1	0.0	0.0	0.0	3.0	74.9
3 M HOT HCl (70°C)	Rinse water 4 (25°C)	7.7	0.0	0.0	0.0	0.5	9.1
	Eluant 4 (water - 80°C)	5.2	12.5	86.4	83.9	72	14

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

4.2.3 PGMs in the pre-treatment solution*

Analysis of the pre-treatment solution showed only trace elements of Pt, Pd and Au and can be seen in Table 4.31.

Table 4.31: PGMs in pre-treatment solution after pre-treatment

		Pre-treatment			Concentration (mg/L)			
Nr	Exp	NaOH (g)	NaCN (g)	Temp (°C)	Pt	Pd	Au	Cu
1	N	0.22	0.8	25	0.03	0.06	0.01	
2	A	0.22	0.8	25	0.02	0.04	0	
3	B	0.8	0.11	25	0	0.12	0	
4	C	0.8	0	25	0.04	0.12	0.03	
5	D	0.22	0.8	25	0.08	0.09	0.19	
6	E	0.22	0.4	25	0.04	0.06	0	
7	F	0.22	0.8	25	0	0.08	0.02	952
8	G	0.22	0	25	0.07	0.09	0.02	49
9	H	0.22	0.8	25	0.04	0.04	0.01	
10[+]	I	0.22	0	25	0.16	0.29	0.04	37
11	J	0.22	0.8	25	0.08	0.18	0.03	651
12	K	0.22	0.4	25	0.00	0.00	0.11	
13	L	0.22	0	25	0	0	0	
14	M	0.11	0.8	25	0	0	0	
15	N	0.22	1.6	25	0	0	0	
16	O	0.22	0	25	0	0	0	
17	P	0.22	0.8	25	0	0	0	
18	Q	0.22	0.4	25	0	0	0	
19	R	0.22	1.2	25	0	0	0	
20	S	0.22	1.2	25	0	0	0	
21	T	0.22	1.6	25	0	0	0	
22	U	0.44	0	25	0	0	0	
23	V	0.44	0.4	25	0	0	0	
24	W	0.44	0.8	25	0	0	0	
25	X	0.44	1.2	25	0	0	0	
26	Y	0.66	0.4	25	0	0	0	
27	Z	0.66	0	25	0	0	0	
28	AA	0.66	0.8	25	0	0	0	
29	AB	0.66	1.2	25	0	0	0	
30	AC	0.44	1.6	25	0.01	0.06	0.79	
31	AD	0.66	1.6	25	0.05	0	0	
32	AE	0.66	1.2	25	0.05	0	0	
33[++]	AK	0.22	0.8	25	0.69	0.95	0.2	

[+]Slightly higher than normal PGMs measured in the clean water samples indicating a possibility of a small amount of contamination in the samples.

[++]Higher initial Pt and Pd loading on the activated carbon (Table 4.23)

* Novel contribution - Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, Factors affecting the elution of Pt, Pd and Au cyanide from activated carbon. Submitted for publication, Hydrometallurgy.

The highest concentration of platinum and palladium found in the pre-treatment solution was 0.69 mg/L for Pt and 0.95 mg/L for Pd and is associated with the activated carbon, that was loaded to a higher PGM loading (3436 mg/kg Pt and 3625 mg/kg Pd). The majority of the experiments were completed with activated carbon with a significantly lower PGM loading (≈ 650 g/t of Pt, Pd and Au each), which showed a maximum concentration of 0.16 mg/L for Pt, 0.29 mg/L for Pd (Experiment 10) and 0.79 mg/L for Au (Experiment 30). In total this represents a maximum loss of 0.15% for Pt, 0.28% Pd (Experiment 10) and 0.6% Au to the pre-treatment solution. For the higher loading on the activated carbon, which is expected to be a better representation of plant conditions (Experiment 33), 0.07% Pt, 0.11% Pd and 0.12% Au reported to the pre-treatment solution. Jeffrey et al. (2009) reported poor elution of gold in the pre-treatment solution with a large peak followed by a typical tail when the distilled water was introduced. Although the fractional loss is lower for the cases with higher initial loading, the loss in revenue is still greater and dictates the need for recycling (possibly to the leaching section) of the pre-treatment solution.

It is important to note that PGM concentrations in the pre-treatment solution are similar to the recoverable PGM concentrations in the initial cyanide leach solution (Mpinga et al., 2012). Considering this, these amounts were then considered significant and the factors influencing these concentrations in the pre-treatment solution were investigated.

The two most plausible explanations that were considered first were the influence of the pre-treatment concentrations on the desorption of the PGMs or simply a washing effect of lightly adsorbed PGMs from the carbon surface.

The cyanide concentration was found (section 4.2.1.3) to have a significant influence on the elution of PGMs and the PGM concentration was therefore plotted against the cyanide concentration and is shown in Figure 4.73.

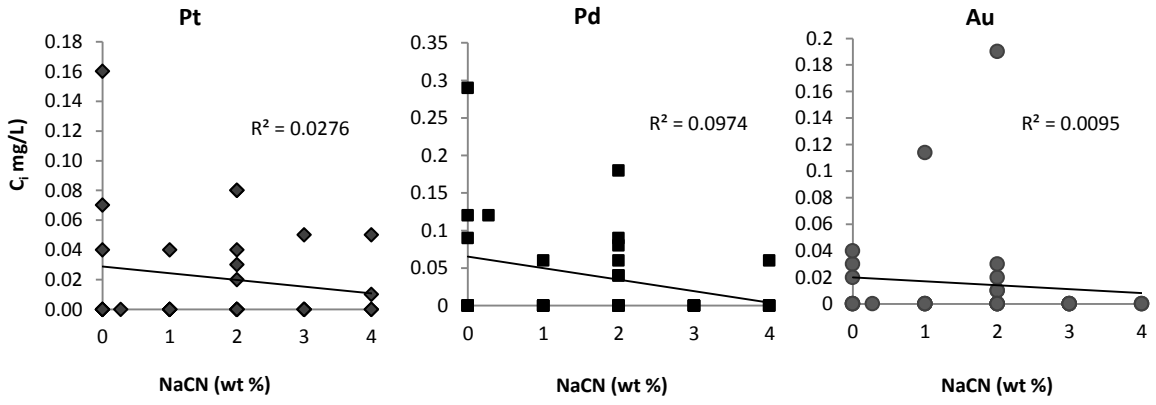


Figure 4.73: Pt, Pd and Au concentration vs the cyanide concentration in the pre-treatment solution

From the plotted data in Figure 4.73 no correlation could be found between the NaCN concentration and the amount of PGMs eluted afterwards. To confirm this, and to incorporate the possible contribution of the NaOH, which was not included in Figure 4.73 above, the data were paired and the PGM concentration was plotted again according to:

- Cyanide concentration at constant NaOH concentration
- NaOH concentration at constant cyanide concentration

No correlation between the pre-treatment NaCN or NaOH concentration and the PGM concentration could, however, be determined and it is therefore concluded that these concentrations have no effect of on the amount of PGMs that are desorbed during the pre-treatment step and another mechanism must therefore be responsible. The plotted data can be seen in Appendix A.

Van Deventer and Van der Merwe (1994) observed that gold would more readily desorb from the activated carbon when the adsorption time was shorter and that the process was more sensitive to the adsorption time under conditions that would favor adsorption rather than desorption, as in the case of weak cyanide pre-treatment conditions. In other words, if the adsorption time is short, which would result in the majority of the gold being distributed on the carbon surface (also in the case of low gold loadings according to Vegter (1992) and Pleysier et al. (2008)), the gold would desorb more readily from the carbon surface even under conditions that do not favour the desorption process. The variability in the PGM concentration in the pre-treatment solution is therefore attributed to the distribution of the PGMs on the carbon particle, and even though very small, a certain amount of these PGMs would readily desorb or wash off the carbon. This conclusion is supported when considering that the PGMs in the pre-treatment solution increased from an average of 0.02 and 0.04 mg/L for Pt and Pd to respectively 0.69 and 0.95 mg/L Pt and Pd when the PGM loading on the activated carbon increased. Furthermore, a correlation was found between the amounts of Pd and Pt in the pre-treatment solution, as shown in Figure 4.74, indicating that as the amount of Pt increased, so did the Pd. The average quantities were found to be in the order of

$$Pd > Pt > Au$$

which is the direct opposite order of the affinity of activated carbon for PGMs as found by Mpinga (2012).

$$Au(CN)_2^- > Pt(CN)_4^{2-} > Pd(CN)_4^{2-} > Ni(CN)_4^{2-} > Cu(CN)_3^{2-}$$

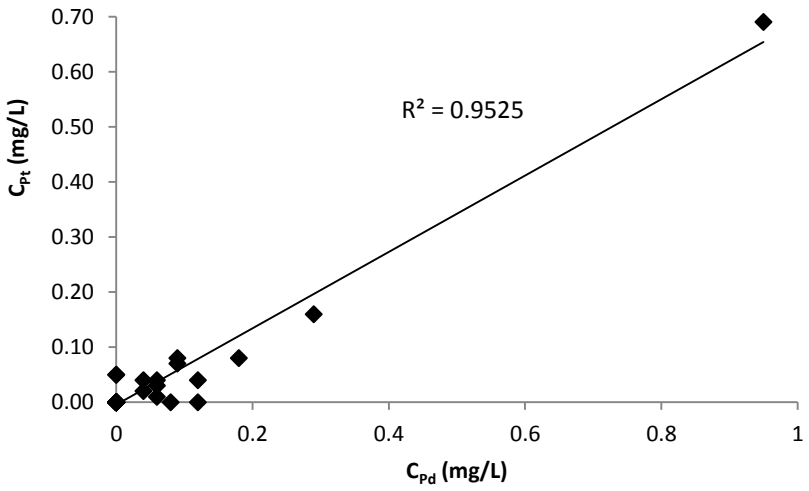


Figure 4.74: Pt vs Pd concentration in the pre-treatment solution.

In comparison to the PGMs, copper, however, did show a correlation with the NaCN pre-treatment, as can be seen in Figure 4.75. More Cu desorbed in the pre-treatment solution as the cyanide concentration increased. The reason for the behaviour is related to the different copper cyano complexes forming with different cyanide concentrations and each with different affinities for the adsorption onto carbon (section 2.6.1).

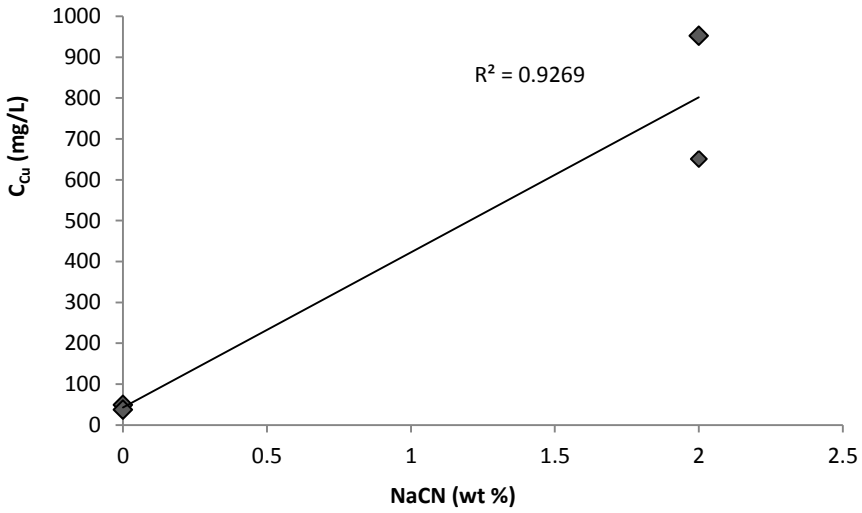


Figure 4.75: Cu concentration vs the cyanide concentration in the pre-treatment solution

The temperature of the pre-treatment was found to have an effect on desorption of Pt and Pd and to a much lesser extent on Au as indicated by Figure 4.76. This result was expected and corresponded to the findings in all of the previous sections, which indicate that Pt and Pd elute at lower temperatures than Au. At 80°C the amount of Pt and Pd reporting to the pre-treatment solution increased to approximately 8%, while the gold loss increased to only 0.8% at 80°C. A similar trend with temperature is seen when the pre-treatment is stirred at 200rpm and also when not stirred (Figure A.136 and Table A.36 in Appendix A.)

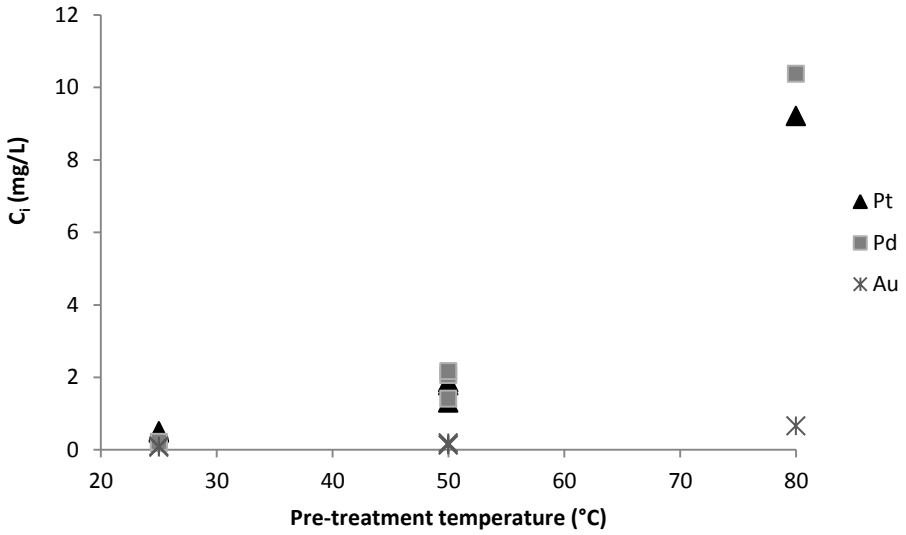


Figure 4.76: PGMs reporting to the pre-treatment solution with rising temperatures at a stirring rate of 40rpm (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH)

4.2.4 Recovery

In a counter current adsorption process, it is important that unloaded carbon with a high activity (carbon after elution) is contacted with the tailings stream in the last adsorption stage in order to remove the last trace amounts of PGMs. This is because the amount of PGMs on the carbon affects the rate of adsorption onto that carbon. The last CIP adsorption stage is therefore most critical, because any PGMs that are not extracted there will be lost to the tailings. Therefore, in order to consistently achieve low barren losses, it is important to maintain a low concentration of PGMs on the carbon fed to the last stage, which is achieved by a high recovery in the elution stage and means the carbon must always be eluted efficiently. When considering the application of this to the CIP adsorption of Au, Fleming (2011) found, by increasing the amount of gold on the eluted carbon, that is recycled to the adsorption section, from 0 to 50 g/t, gold soluble losses increase by 370%.

Expected grade vs recovery curves (calculated from the elution recovery curve shown in Figure 4.64) for a Pt and Pd carbon loading of 3436 mg/kg Pt and 3625 mg/kg Pd are shown in Figure 4.77.

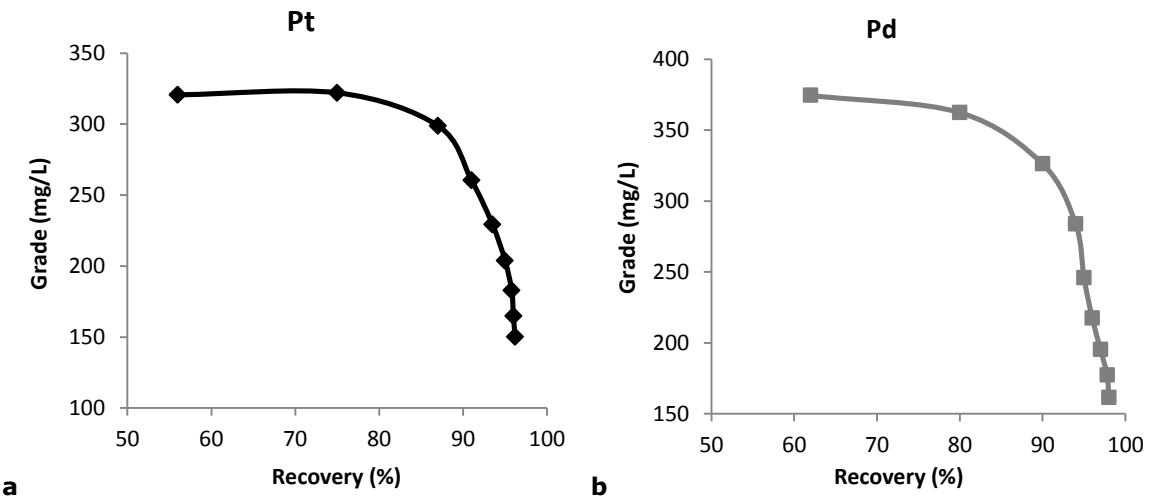


Figure 4.77: Upgraded solution vs the elution recovery. (Carbon loading: 3625 mg/kg Pd, 3436 mg/kg Pt after pre-treatment with 2% NaCN and 0.55% NaOH at 80°C)

Ideally, the desired elution recovery versus the grade for further processing alongside the upgrading ratio should be considered during the design stages of the plant. According to Fleming et al. (2011), the up-grading ratio has a significant impact on the plant performance and when carefully considered during the design stages can result in important advantages. Increasing the up-grading ratio and lowering the carbon advance rate is beneficial, as it reduces the size of the elution and regeneration plants and lowers both capital and operating costs. But operating the plant at higher gold loadings slows the rate of adsorption of gold cyanide onto carbon, results in a larger Metal in Process (MIP) amount and can potentially increase the gold losses in the barren solution. It is possible to achieve both high gold loading on the carbon (7000 g/t) and low barrens (0.002 mg/L) by installing more CIP tanks. In addition, the gold losses can also be minimized by increasing the elution recovery, but this will decrease the grade for further processing (increased flow). To arrive at an economic optimum design, an analysis can be made of the once-off capital cost penalty of an extra CIP tank and larger downstream equipment for further processing versus the lifetime operating cost benefit of a lower carbon flow to elution and regeneration and lower gold losses to the tailings.

Chapter 5*

Mathematical modelling of Pt elution

5.1 Introduction

The stripping of adsorbed tetracyanoplatinate(II) ($[Pt(CN)_4]^{2-}$) from activated carbon has been shown in the previous section to consist of a two step batch process, which involves the pre-treatment of the metal-loaded activated carbon with a relatively strong sodium cyanide and sodium hydroxide solution prior to the elution step with de-ionized water at 80°C. This section attempts to model this process and to fundamentally describe the mechanism of platinum elution from activated carbon. The benefits of fundamentally understanding this process can ultimately lead to improved elution, better process control, shorter elution times and smaller elution columns or assist in the development of a continuous elution process.

The elution of $[Pd(CN)_4]^{2-}$ has been found to closely resemble that of $[Pt(CN)_4]^{2-}$ and points towards to a similar elution mechanism for Pd. The focus of the current chapter will, therefore, only be to model Pt elution and not that of Pd as well.

5.2 Gold elution modelling

Since no fundamental studies regarding the elution of platinum cyanide from activated carbon exist in open literature, the AARL process, and to a lesser extent the Zadra elution process, were studied as basis for the successful modelling of the platinum elution process.

Adams and Nicol (1986) modelled the Zadra elution process and assumed the gold cyanide diffuses to an interface where equilibrium with the liquid phase exists. From the interface the gold then diffuses through a liquid film into the bulk of the liquid. A linear isotherm was used to describe the equilibrium, which was later shown by Adams (1990) to be applicable only for very short columns and high flow rates. The intra-particle diffusion was described by a single average mass transfer coefficient.

A model of the AARL process was developed by Van der Merwe and Van Deventer (1990), who used the same fundamental model to describe the AARL and the Zadra elution processes. This model is similar to the adsorption model developed by Van Deventer (1984) and incorporates a macro pore mass balance equation, a micro pore mass balance, a mass balance at the external particle surface, a mass balance over the interparticle solution and a Freundlich isotherm (Eq. 5.1) to describe the equilibrium. The partial differential equations were solved with a 4^{th} order Runga-Kutta routine.

* Novel contribution – not published to date

$$Q = A.C^n \quad (5.1)$$

Importantly, A was found to change as conditions during the elution process changed and was subsequently written as a function of temperature, pH, cyanide concentration and individual cation (K^+,Na^+) concentration. From this model, Van der Merwe and Van Deventer (1990) concluded that the shape of the gold elution profile for an AARL process is a function mainly dependent on the removal of the cations from the activated carbon, that had been adsorbed during the pre-treatment stage. It was also concluded that, although the cyanide pre-treatment plays a very important role in elution efficiency and determines the height of the elution peak, the small amount of free cyanide, that is carried over from the pre-treatment step and present during the initial stage of the elution, is of little importance. The dependence of A on the system conditions is not an isolated case. Woollacott and Nino de Guzman also found A to be dependent on oxygen and cyanide concentration in gold cyanide adsorption systems, while Öser et al. (1999) stated that A is a function of the energy of adsorption and temperature and a measure of adsorption capacity, while n represents adsorption intensity.

Stange (1991) simulated the wash process as a binary system, containing Na^+ and aurocyanide and described the rate of desorption as a rate expression with kinetic and equilibrium parameters and assumed that film transfer is the rate limiting process for both sodium and gold. With a constant value for the gold mass transfer constant, and the equilibrium parameter for gold assumed to be a function of the sodium solution tenor, an acceptable fit with industrial elution data was obtained. When the predictive nature of the model was tested, however, it was found to be rather insensitive towards an increase in the sodium ion concentrations in the eluant, and this insensitivity was ascribed to incomplete model development.

In another study, Banini and Stange (1994) described the AARL elution process through equilibrium studies as well as elution kinetic data. A modified Freundlich isotherm for a single component system and a general empirical multi-component isotherm developed by Fritz and Schlunder (1974) for a multi-component system were found to describe the adsorption isotherms the best. The kinetic elution from the activated carbon was described by assuming a packed bed reactor problem with an associated mass balance equation over the carbon particle phase, a mass balance over the external particle phase, which incorporated the film transfer coefficient and surface diffusion and a reactor mass balance, which was a full plug flow model. These three mass balance equations were solved simultaneously with the modified Freundlich isotherm using the method of characteristics and the results compared to experimental data. It was found that inclusion of the surface diffusion coefficient led to less accurate modelling, and only the film transfer coefficient as the rate determining factor gave accurate prediction of the experimental data. Although a good fit to the data presented was found, a full plug flow model, which is a hyperbolic differential equation, was assumed and therefore resulted in a function, which only described the tail of the typical bell shaped elution profile without predicting the peak or the front part leading up to the peak. The model also did not consider the influence of ions like Na^+ and assumed that the influence of these ions was negligible due to the high purity of distilled water used as eluant. These ions were, however, considered to be important as they affect the

equilibrium behaviour of gold and influence the kinetics of elution. The model was found to be sensitive to the film transfer coefficient.

Optimization and control of the elution process demand that mathematical models be developed. As no model currently exists for Pt elution, the aim here is to develop such a model and to determine the appropriate rate constants through fitting of the models to experimental results.

5.3 System definition

The experimental method was described in detail in Chapter 3 and involved contacting a synthetic solution of platinum-, palladium- and gold cyanide with activated carbon for 65 hours by means of the traditional bottle-on-rolls method for adsorption. The pre-treatment step occurred by stirring the loaded activated carbon in glass beakers in a NaCN and NaOH solution at room temperature. After the pre-treatment the carbon was separated from the solution by decanting, and the excess solution removed by filtering. The carbon was then immersed into the temperature controlled glass column containing half a column of eluant (water) at the elution temperature. A schematic of the experimental set-up and modelling domain is shown in Figure 5.78 with the domain parameters given in Table 5.32. The starting time for the elution was taken as the moment when flow of eluant was introduced. Samples were taken at the column outlet and analysed with ICP-AES. A typical elution profile can be seen in Figure 5.79.

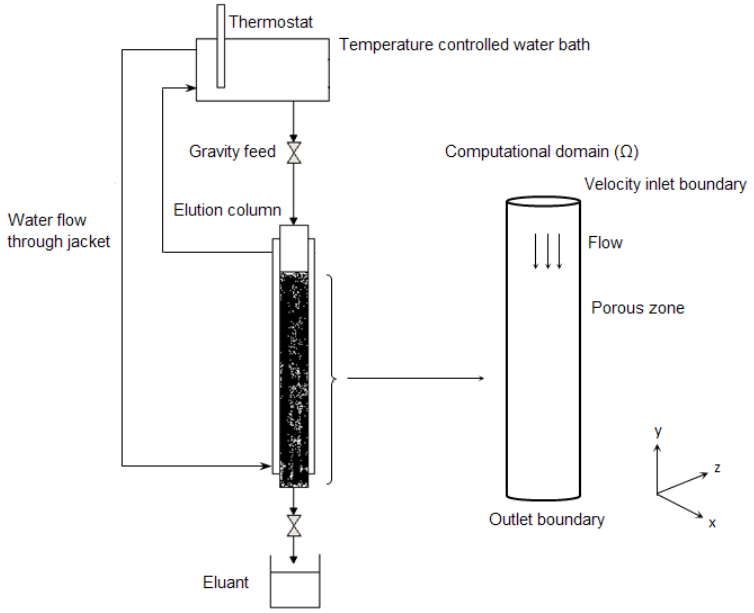


Figure 5.78: The experimental set-up with the corresponding computational domain (Ω)

Table 5.32: Column and elution parameters

Parameter	Symbol	Unit	Value
Column diameter	ø	mm	12
Column length	L	mm	210
Water velocity at inlet	V_{inlet}	mm/s	0.11
Carbon particle diameter	d_{AC}	mm	2.3
Porosity	ε		0.4
Elution temperature	T	°C	80

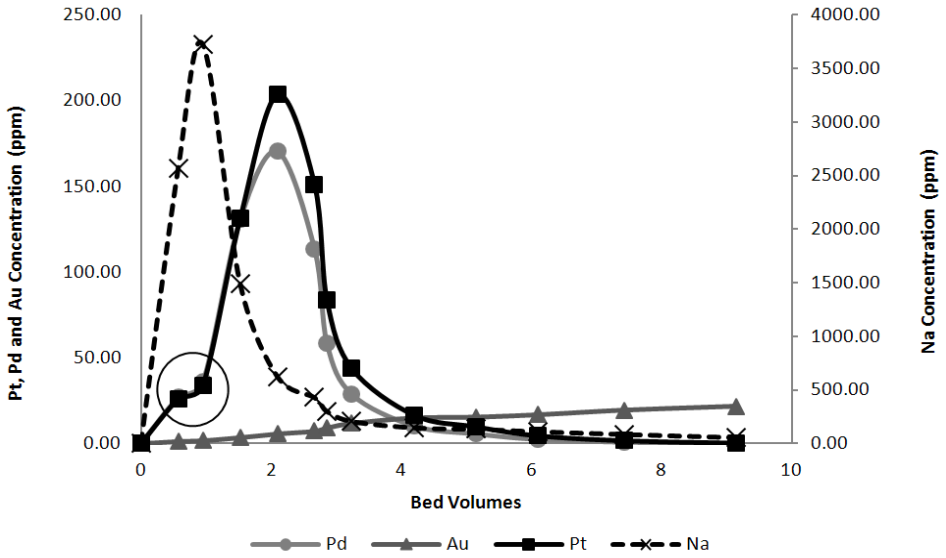


Figure 5.79: The elution of $[Pt(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$, $[Au(CN)_2]^{2-}$ and Na^+ ions from activated carbon (650g/t of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (2 wt% NaCN, 0.6 wt% NaOH) at 80°C.

After analysing the experimental data and plotting elution profiles certain features were evident, that were deemed important in the understanding of the elution mechanism, and which therefore needed to be incorporated into the numerical model.

The first involved the explanation and incorporation of the 'slow down' in elution kinetics during the first 1500 seconds and is highlighted by the circle in Figure 5.79, which shows the first sample point to contain 25 mg/L Pt and Pd with the second sample point showing only a minor increase of 5 mg/L to 30 mg/L before a dramatic increase to 130 mg/L in the third sample. As all of the 37 elution profiles showed this effect, it was considered to be an actual occurrence and therefore an actual temporary decrease in elution kinetics. This phenomenon was also visible in gold elution sample points from literature references (Davidson et al., 1979, Van der Merwe, 1991), but is not particularly discussed or even taken into consideration, except by Van der Merwe and Van Deventer (1990), who showed the elution of gold was suppressed in the presence of 2000 ppm K+, but on making a step change to 0 ppm and following removal of all K+, the rate of elution increased. The second challenge was to determine the parameters that effect the position of the peak, and also the extent and position of the reduction in elution rate when loaded carbon was

treated with an identical pre-treatment solution (2 wt% NaCN at 0.6 wt% NaOH) and then eluted at similar conditions (80°C with distilled water).

5.4 Theoretical approach

The dimensionless numbers for the specific column and following elutions were calculated and are shown in Table 5.33. Schmidt numbers were calculated from the diffusion coefficients of Na and $Pt(CN)_4^{2-}$. While the diffusion coefficient of Na^+ could be obtained from literature (Bastug and Kuyucak, 2005), the value for $Pt(CN)_4^{2-}$ had to be estimated using Eq. 5.2 (Grunwald, 1989). The validity of Eq. 5.2 was tested by calculating the diffusivity coefficients of a number of species and compared to literature values of which an estimated average error of 14% was found (Table A.40 in Appendix A).

$$D_i = \frac{(1.7e-7)T\mu}{M^{0.41}} \tag{5.2}$$

Schmidt numbers relate the diffusion due to momentum to the mass diffusivity. The larger this number, the less mass diffusion occurs with Shaw and Hanratty (1977) indicating a number of 2300 to neglect the diffusion in two directions, but maintaining the diffusion in the third direction across the concentration boundary layer. The degree to which axial dispersion influences the reactor is determined by the Peclet number, and similarly to the Schimdt number, the higher the Peclet number, the less dispersed it is. Peclet numbers to infinity represent ideal plug flow, while Peclet numbers of 0 indicate complete back mixing. According to Dudukovic and Felder (2012), for Peclet numbers greater than 20, the convection diffusion equation is suitable and ideally suited to model the behaviour of packed bed reactors.

Table 5.33: Dimensionless numbers

Dimensionless number	Formula	Value
D_{Pt} (m^2/s)*	$D_i = \frac{(1.7e-7)T\mu}{M^{0.41}}$	4.36E-10
D_{Na} (m^2/s)**		3E-09
Re	$Re_p = \frac{\rho V d_{AC}}{\mu}$	0.253
Sc_{Pt}	$Sc_i = \frac{\mu}{\rho D_i}$	2294
Sc_{Na}		333
Pe_{Pt}	$Pe_i = ReSc_i$	580
Pe_{Na}		84
Column/particle diameter	$\frac{\emptyset}{d_{AC}}$	5.2

*calculated by Eq. 5.2 as per Grunwald (1989)

** Bastug and Kuyucak (2005)

Considering the relatively low column to particle diameter ratio of 5.2, the possible column was evaluated for the influence of wall effects. Larger diameter columns packed with the same activated carbon were therefore evaluated and the porosity found to be similar to that of the column used for modelling (Figure A.140 in Appendix A). The wall effects were therefore deemed to be small and not included in the model.

The model for the elution of platinum cyanide from activated carbon is shown graphically in Figure 5.80. A solution mass balance over each of these sections is given by:

$$M_{j-1} + N = M_j \tag{5.3}$$

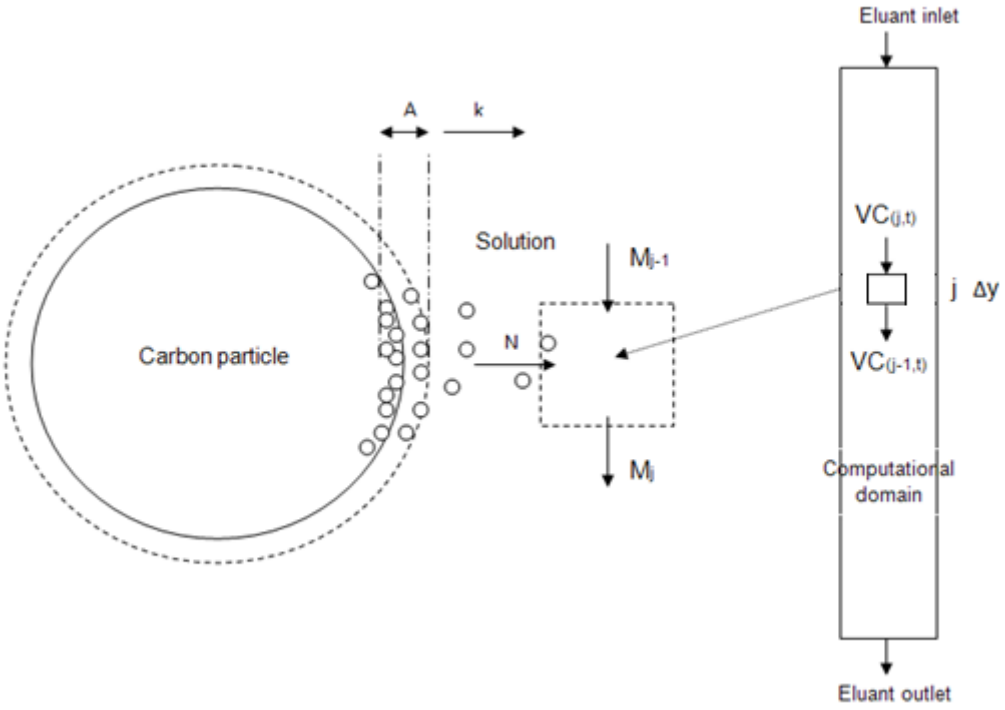


Figure 5.80: Graphical representation of the elution modelling of platinum cyanide from activated carbon

The two basic equations that govern the laminar flow of liquid through a bed of packed bed of solid particles are the Convection-Diffusion equation (5.4) and the Navier-Stokes equation (5.5) for an incompressible fluid.

$$\frac{\partial}{\partial t}(c) + V\nabla c = D\nabla^2 c + N_i \tag{5.4}$$

$$\frac{\partial}{\partial t}(\rho V) + \nabla \cdot (\rho VV) = -\nabla p + \mu\nabla^2 V + \rho g + F \tag{5.5}$$

The value for F in Eq. 5.5 represents the external body forces due to the mass source introduced (F_m) as well as to compensate for the porous media (F_{porous}) (Fluent 12.0, 2009), which is modelled

by Darcys Law. Darcy's law is a proportional relationship between the velocity field and the pressure gradient and is valid for $Re_p < 1$ as in this case (Table 1). This method is described as the penalization approach (Cimolin and Discacciati, 2013, Bruneau and Mortazavi, 2008) and is used in many practical applications and most software packages.

$$F_{porous} = -\left(\frac{\mu}{\alpha} V_y\right) \tag{5.6}$$

A general assumption related to the fluid flow is:

- All processes within the column are isothermal. The elution column is assumed to be at a constant temperature of 80°C, no additional equation for energy conservation is solved and all constants determined are therefore applicable to an elution column at 80°C.

Platinum mass balance

To calculate the rate at which platinum cyanide desorbs from the activated carbon into the solution, the following assumptions were made:

- All metals are on the surface of the activated carbon and not diffused into the micropore structure of the activated carbon. SEM-EDX analysis (Snyders et al. 2014) indicated that the Pt distribution on the surface of the carbon was approximately equal at a carbon loading of 2140 mg/kg, while at a higher loading of 16800 mg/kg, the Pt concentration inside the pores was considerably higher. This is therefore in agreement with Pleysier et al. (2008) and Vegter (1992) who showed that at Au loadings below saturation, as well as in cases where adsorption amounts to days rather than weeks, Au adsorption predominantly takes place at the external surface of the carbon particles. This concurs with the results of Banini and Stange (1994) who found their AARL model to be insensitive to the surface diffusion constant and concluded film transfer to be the rate limiting step.
- The metal concentration on the carbon surface and in the liquid at the carbon/liquid interface is in equilibrium and diffuses from this interface through a liquid film into the bulk of the liquid (Adams and Nicol, 1986). This equilibrium at the carbon/liquid interface can mathematically be expressed by a Freundlich isotherm (Eq. 5.1), with the equilibrium constant A being dependent on the cations in the system (Van der Merwe, 1991). The Freundlich isotherm has also been found to describe Pt equilibrium adsorption rather well, as opposed to the Langmuir isotherm (Snyders et al. 2014) and was therefore deemed appropriate in this case.
- The diffusion through the liquid film is described through the well known mass transfer equation

$$N = k(C - C_L) \tag{5.7}$$

By substituting Eq. 5.1 into Eq. 5.7, the Pt mass flux can be written in terms of the amount of Pt (Q_{Pt}) that is on the activated carbon and closely resembles the rate expression derived by Stange (1990).

$$N_{Pt} = kBQ_{Pt}^{\frac{1}{n}} - kC_{L_{Pt}} \quad (5.8)$$

where $B = \frac{1}{A^{\frac{1}{n}}}$

Substitution of Eq. 5.8 into the general form of the mass conservation equation (Eq 5.3) yields:

$$\frac{\partial C_{Pt}}{\partial t} + V\nabla c_{Pt} = D_{Pt}\nabla^2 c_{Pt} + kBQ_{Pt}^{\frac{1}{n}} - kC_{L_{Pt}} \quad (5.9)$$

The Pt mass balance for the amount of Pt left on the carbon at a time (t) is given by Eq 5.10:

$$\frac{Q_{Pt,t}m_{AC}}{BV} - N_{Pt}\Delta t = \frac{Q_{Pt,t+\Delta t}m_{AC}}{BV} \quad (5.10)$$

Na^+ cation elution and water balance

Early on in the development phase of the model, it became clear that the elution of Na^+ had to be incorporated into the model to describe the behaviour of Pt elution effectively. Although the Na^+ was measured during each step in the process (Appendix B), the variation (or accuracy) of these data points was such, that no conclusions could be drawn regarding the extent of adsorption during each loading experiment and subsequent pre-treatment step. It also certainly did not allow for accurate mass balance calculations to develop and validate a mathematical model. From the Na^+ data available, it was found that a reasonable fit could be obtained by modelling the Na elution as a constant elution rate and it subsequently became clear that the Pt elution could almost be perfectly described if the Na^+ model fitted the experimental data. As the main objective was to investigate and model platinum elution, the Na^+ adsorption and elution was not further researched (which would have required additional dedicated Na experiments) and the Na^+ elution was simply modelled as a constant elution rate (Eq 5.11), which was determined through fitting.

$$N_{Na} = K_{Na} \quad (5.11)$$

$$\frac{Q_{Na,t}m_{AC}}{BV} - N_{Na}\Delta t = \frac{Q_{Na,t+\Delta t}m_{AC}}{BV} \quad (5.12)$$

Substitution of Eq 5.11 into Eq 5.3 yields Eq 5.13:

$$\frac{\partial C_{Na}}{\partial t} + V\nabla c_{Na} = D_{Na}\nabla^2 c_{Na} + K_{Na} \quad (5.13)$$

As no water is eluted from the activated carbon, unlike the case for Pt and Na, Eq. 5.3 is simplified to yield Eq. 5.14

$$\frac{\partial C_{water}}{\partial t} + V\nabla c_{water} = 0 \quad (5.14)$$

To analyse the problem mathematically, computational fluid dynamics (CFD) was chosen to solve the associated flow- and mass balance equations. CFD is a numerical tool to analyze flow and heat transfer phenomena as well as coupled chemical reactions in engineering processes. A commercial CFD code *Fluent 12.1.4*, coupled with user defined functions (created in C++), was used to solve the cases.

Boundary conditions

A cylindrical column with dimensions of 12 mm internal diameter with a length of 210 mm corresponding to the carbon filled section of the experimental laboratory column (Figure 2) was developed and divided into 25252 discrete cells (the mesh) making use of a cooper (uniform) meshing scheme along the length of the column. The dimensions of the column corresponded to the 12 mm diameter gold elution columns with 9 g of activated carbon used by Van Deventer and Van der Merwe (1990), Van der Merwe and Van Deventer (1990) and Van Deventer and Van der Merwe (1994).

The water inlet superficial velocity was specified at between 0.09 and 0.15 mm/s (inlet boundary condition) depending on the flow rate of the specific experiment and assuming laminar flow (Table 5.32). The Pt and Na ions on the activated carbon were assumed to be distributed evenly throughout the column at the start of the elution. For the model, this was achieved by dividing the total mass of Pt and Na adsorbed onto the activated carbon by the volume of the column in order to determine the Pt and Na loading per unit volume, which was then assigned to each cell in the modelling domain as a starting boundary condition for the mass source terms.

Since the elution column is assumed to be at a constant temperature of 80°C, no additional equation for energy conservation is solved, and all constants determined, are therefore applicable to an elution column at 80°C.

The governing equations (Eq. 5.5, 5.9, 5.10, 5.12, 5.13 and 5.14) are solved for the computational domain (Ω) with a pressure based solver, historically developed for low speed incompressible flows as in this case, which solves a pressure correction equation to correct the velocity field calculated by the momentum equation in order to satisfy the continuity equation (Fluent 12.0, 2009). These governing equations are solved repeatedly for each time increment until the solution is converged. First order accuracy is assumed, which states that the cell centre values represent a cell average value and holds throughout the entire cell. First order and second order accuracy (which calculates a gradient over a cell instead of a cell average) showed similar results.

5.5 Model development and fitting of parameters

Numerical values (Figure 5.85 and Figure 5.86) for the constants in Eq. 5.9 and Eq. 5.13 were determined through trial and error and optimised by the least squared error method to provide the best possible fit to several different experimentally determined elution profiles.

The experimental data, that were used for determining the parameters, are shown from Figure 5.81 to Figure 5.84 and Figure 5.87 to Figure 5.88. The first parameter fitting is shown for experiments at similar pre-treatment conditions, but with different platinum loadings on the activated carbon as shown in Figure 5.81.

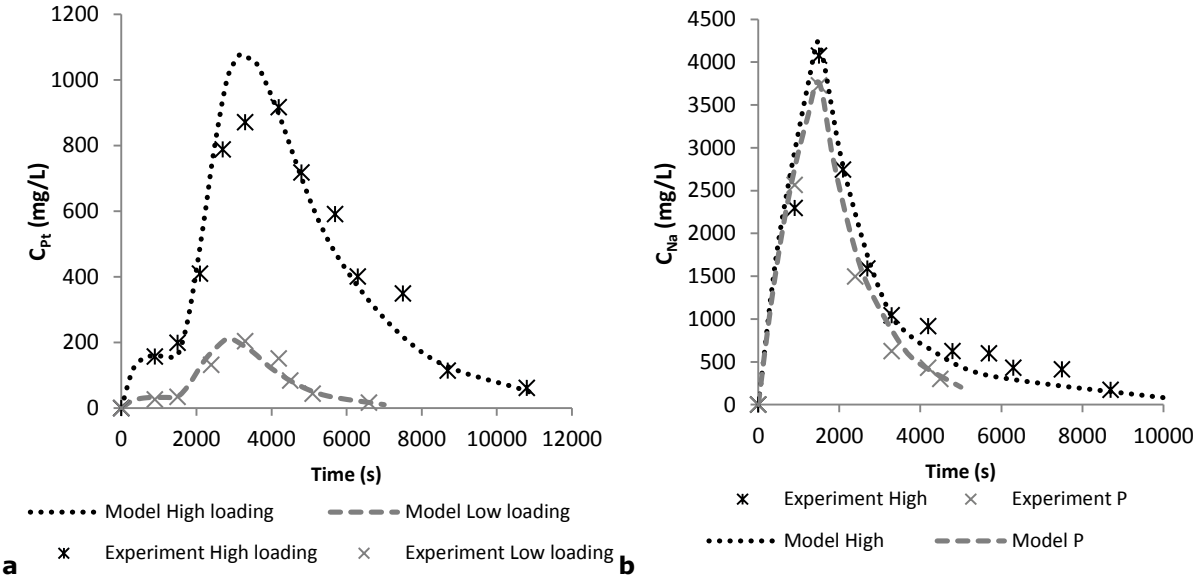


Figure 5.81: Parameter estimation with the elution results from an activated carbon loaded with 3436 mg/kg platinum (Experiment High) and a lower loading of 650 mg/kg platinum (Experiment P) after pre-treatment with 2 wt% NaCN and 0.6 wt% NaOH at 80°C

The parameter fitting also included experiments, that were seemingly completed at similar conditions. The activated carbon loading in both experiments was similar (≈650 mg/kg), both pre-treated with 2% NaCN and 0.6% NaOH and eluted at 80°C, but which resulted in two slightly different shaped profiles. The difference in the shape of the profiles is mainly regarding the position where the 'slow down' in platinum elution occurs and the horizontal position of the peak. Analysis revealed that the Na content for the one experiment was almost double the amount of the other one and the main cause for the different shaped profiles. Figure 5.82 shows the model comparison for these two experiments. Because experiment H contained more Na^+ ions, that needed to be eluted, it depressed the elution of platinum at the start of the experiment more than for experiment P, that contained less Na^+ ions. Although more Na^+ was present, the elution rate of the Na^+ ions was faster for experiment H and since the Na^+ was therefore washed out of the column sooner than for experiment P, the elution of platinum for experiment H was also faster and resulted in a peak towards the left of experiment P. As can be seen from Figure 5.82, the model predicts this behaviour accordingly.

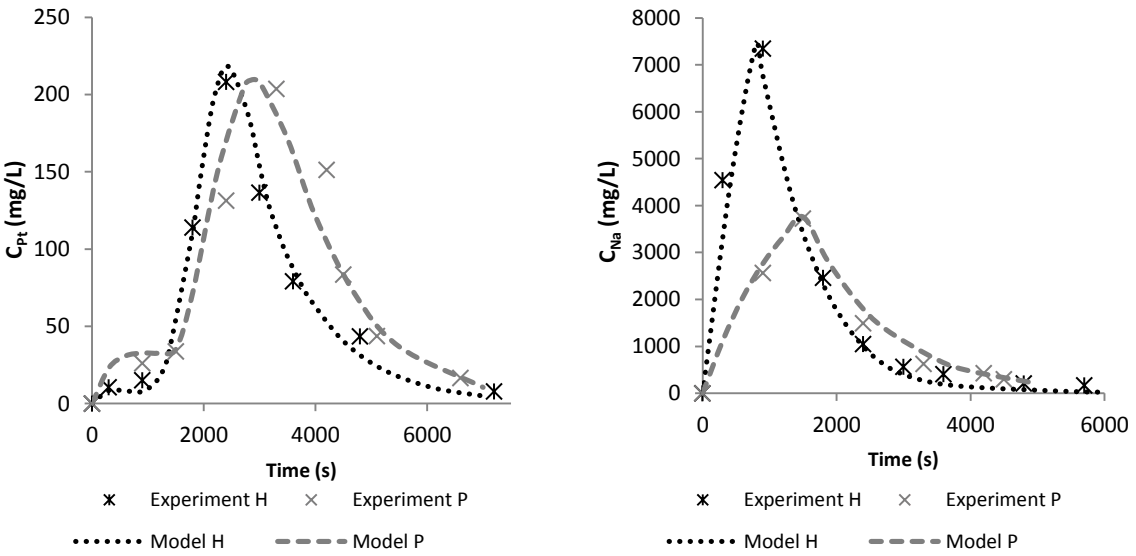


Figure 5.82: Parameter estimation with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 2 wt% NaCN and 0.6 wt% NaOH at 80°C. The main difference is the sodium elution.

Elution experiments, that were pre-treated with higher sodium cyanide and sodium hydroxide concentrations, were also included in the parameter fitting and are shown in Figure 5.83 and Figure 5.84.

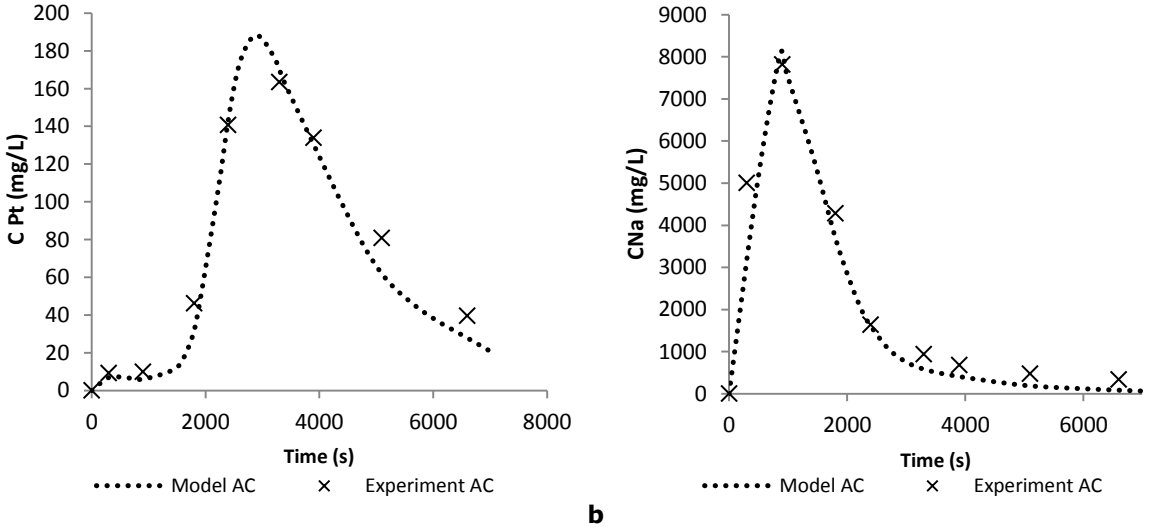


Figure 5.83: Parameter estimation with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 4 wt% NaCN and 0.9 wt% NaOH at 80°C.

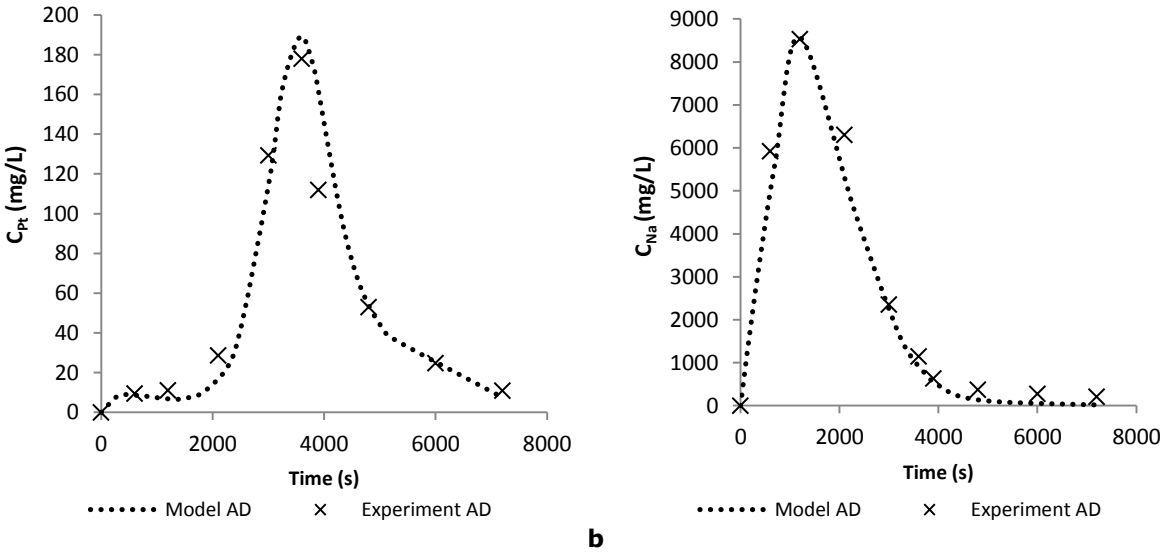


Figure 5.84: Parameter estimation with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 4 wt% NaCN and 1.2 wt% NaOH at 80°C.

To explain the shape of the curve and the 'slow down' in elution kinetics, as previously discussed, instead of single parameter values for the film transfer and equilibrium coefficients, it was rather found that both the film transfer coefficient (k, Eq. 5.15) as well as the equilibrium coefficient B are dependent on the Na^+ concentration and are shown in Figure 5.85 and Figure 5.86. For the film transfer coefficient, this dependency corresponds to previous findings (section 4.2.1.4), which demonstrated a decrease in the platinum elution efficiency as the Na^+ content of the elution water increased. The calculated value of $3.4x10^{-6}$ for the mass transfer coefficient (k) of platinum for Na^+ free water corresponds to the mass transfer coefficient values, as reported by Banini and Stange (1994), of between $0.24x10^{-6}$ and $4.0x10^{-6}$ for gold cyanide elution.

$$k = 3.4x10^{-6}e^{-540Y_{L_{Na}}} \quad (5.15)$$

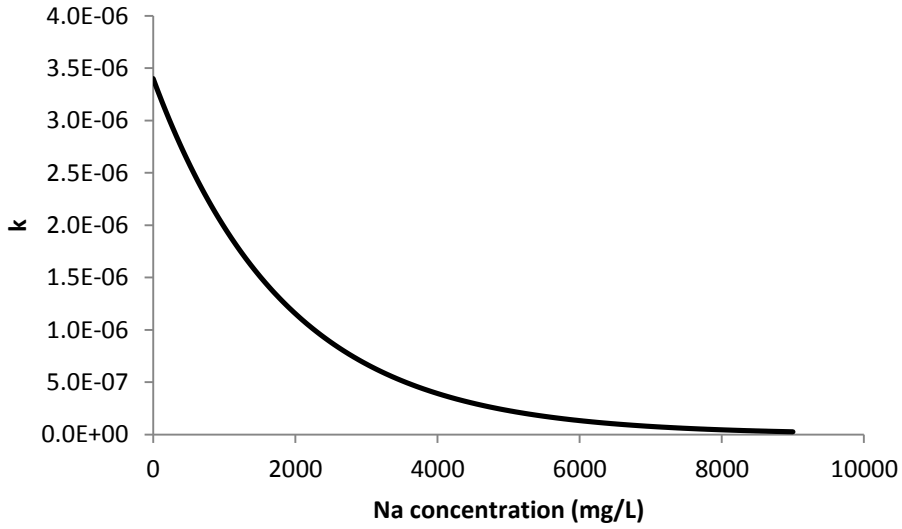


Figure 5.85: The dependency of the film transfer coefficient on the Na^+ concentration/mass fraction in the eluant

The constant B (modified term from the Freundlich Isotherm) was also found to be dependent on the Na^+ cations, but more specifically the Na^+ cations still on the surface of the activated carbon (Q_{Na}). B are represented by Eq. 5.16 and depicted in Figure 5.86. By converting the values found for B back to the equilibrium constant A, values of between 0.004 and 0.02 (depending on the Na^+ content) is found, which essentially indicates that very little to no adsorption will take place at these conditions. This is precisely what is expected since the factors that strongly favour desorption namely cyanide pre-treatment as well as high temperatures are involved.

$$B = 19{Q_{Na}}^{-0.29} - 40 \tag{5.16}$$

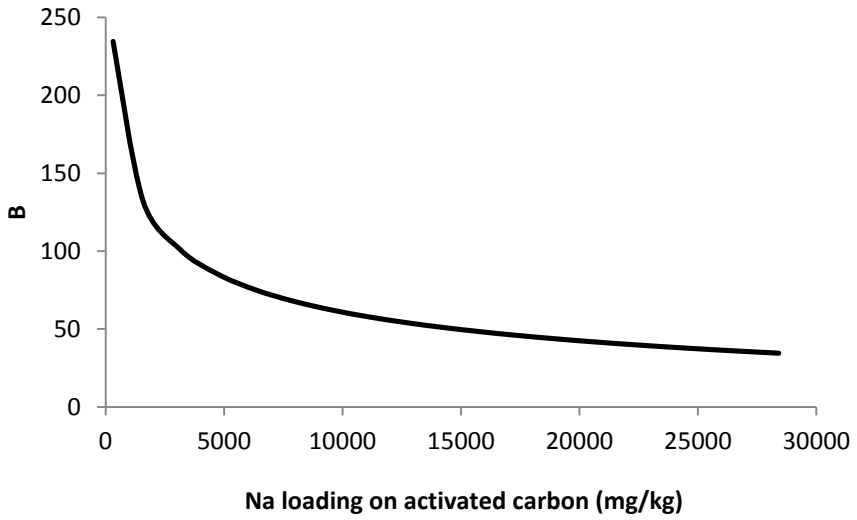


Figure 5.86: The dependency of B on the Na (cations) on the surface of the activated carbon

From both Figure 5.85 and Figure 5.86, the strong sensitivity of the Pt elution on the Na^+ on the surface of the activated carbon and in the eluant is evident. This finding for Pt elution is therefore similar to the experiments performed by Van Deventer and Van der Merwe (1994), which showed that the bulk of the gold desorption only occurs once the cation concentration in the eluant is lowered.

As stated before, the cyanide pre-treatment has a significant influence on PGM elution. Experimentation has shown that the Pt elution recovery increases significantly as the concentration of NaCN in the pre-treatment step is increased from 0 to 2% with 2% been found to be the optimum. Model predictions, as shown in Figure 5.81 to Figure 5.84, have shown to be accurate for NaCN concentrations from 2% to 4%, but in order to model accurately for lower NaCN concentrations, a correction factor to the equilibrium model (B, Eq. 5.16) had to be applied. This corresponds to the finding by Van der Merwe and Van Deventer (1990), who also concluded that the equilibrium term was a function of inter alia cyanide concentration.

Figure 5.87 shows the model results for a NaCN concentration in the pre-treatment step of 0%, which required a cyanide (correction) factor of 0.4 to all terms of Eq.5.16 or the equilibrium term B (derivative of the Freundlich constant A) and Figure 5.88 shows the results for NaCN concentration of 1%, which required a cyanide factor of 0.65. This finding corresponds to both Van Der Merwe

(1991) and Woollacott and Nino de Guzman, who found that the constant A in the Freundlich Isotherm is dependent on the cyanide concentration.

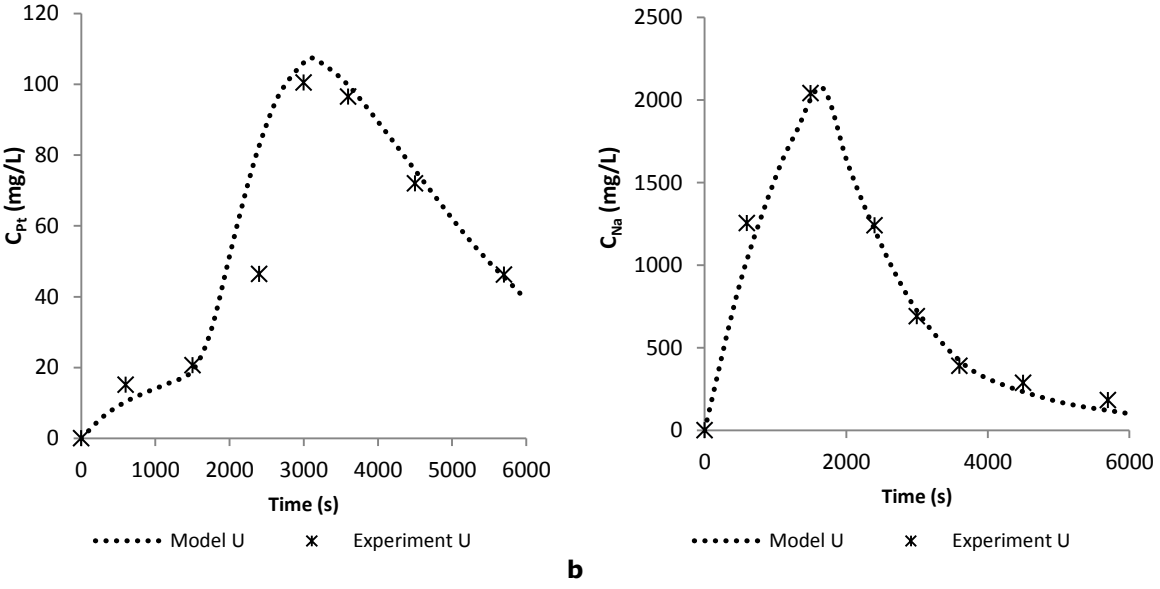


Figure 5.87: Parameter estimation with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 0 % NaCN and 1.2 wt% NaOH at 80°C. A correction factor of 0.4 to the equilibrium term B was applied.

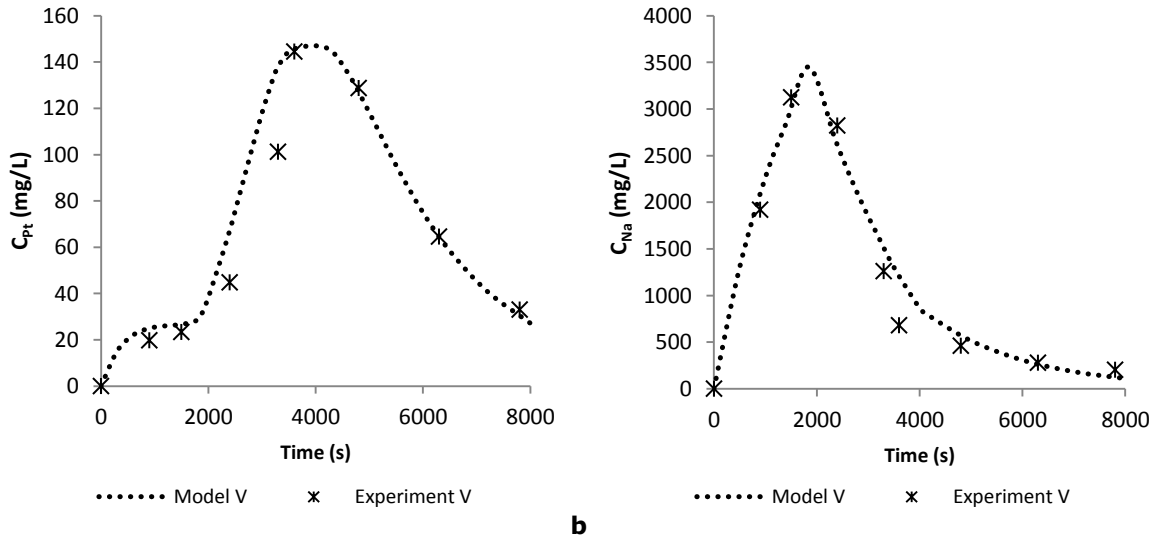


Figure 5.88: Parameter estimation with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 1 wt% NaCN and 1.2 wt% NaOH at 80°C. A correction factor of 0.65 to the equilibrium term B was applied.

The change to the equilibrium constant B with cyanide concentration is shown in Figure 5.89. The film transfer remains as shown in Eq. 5.15 and Figure 5.85 and is not directly affected by the NaCN concentration in the pre-treatment step.

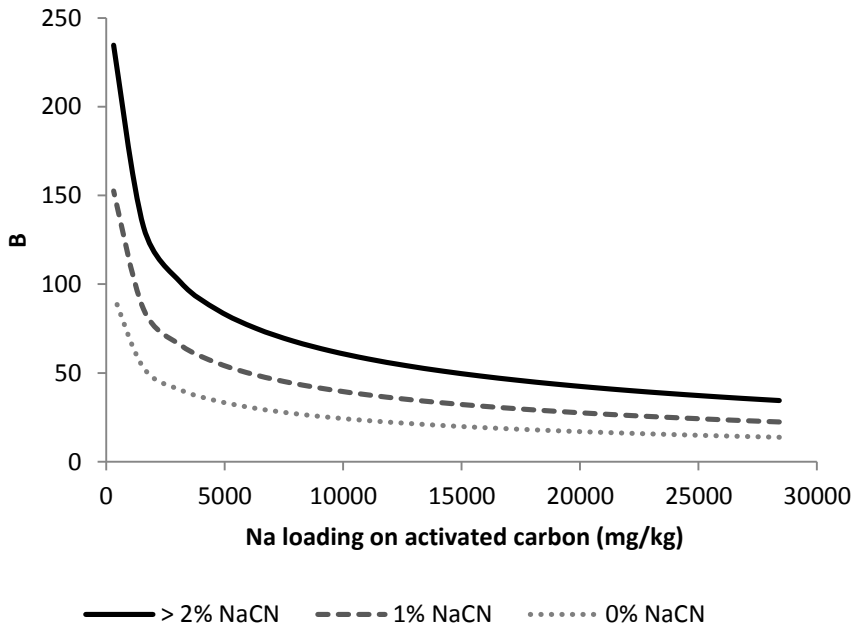


Figure 5.89: The dependency of B on the Na (cations) on the surface of the activated carbon with changing NaCN concentrations in the pre-treatment step.

5.6 Model validation

To verify the proposed parameters, the model was validated against several more experiments shown in Figure 5.90 to Figure 5.94. Each of the experiments the model was evaluated against, resulted in a good fit and the estimated values for the film transfer and equilibrium coefficient were deemed accurate for the elution of platinum cyanide from activated carbon with pre-treatment concentration varying from 0% to 4% NacCN and 0.6% to 1.7% NaOH.

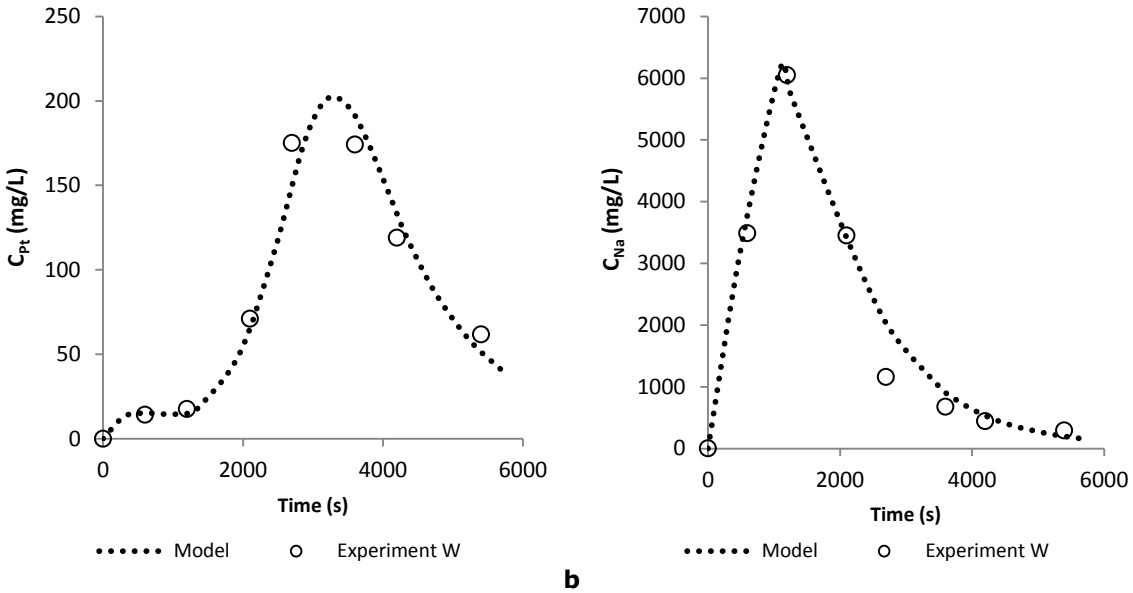


Figure 5.90: The model results compared with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 2 wt% NaCN and 1.2 wt% NaOH at 80°C.

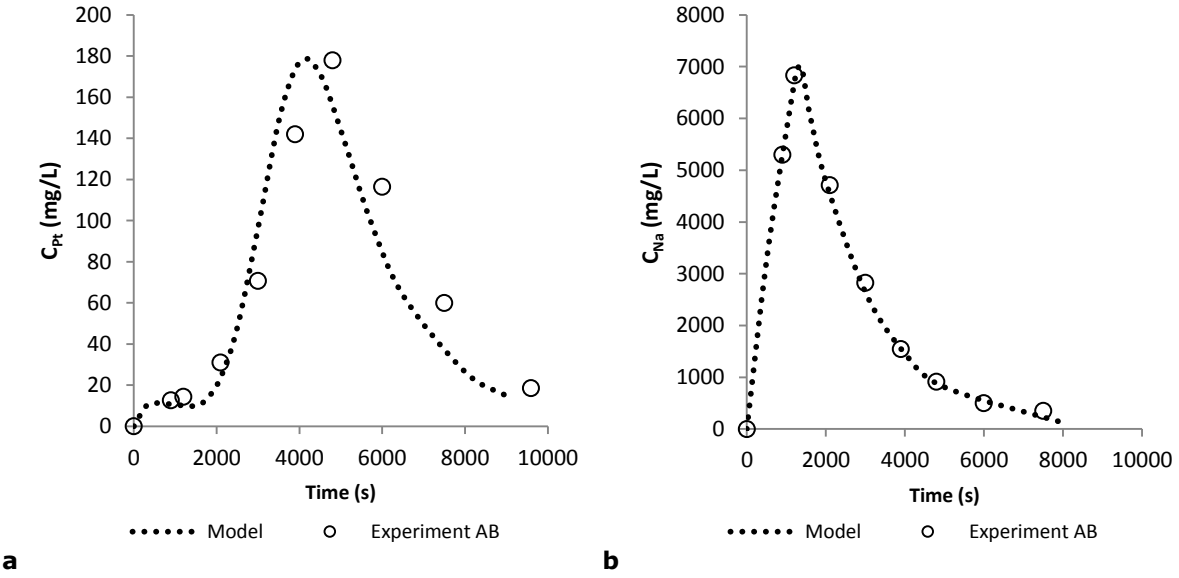


Figure 5.91: The model results compared with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 3 wt% NaCN and 1.7 wt% NaOH at 80°C.

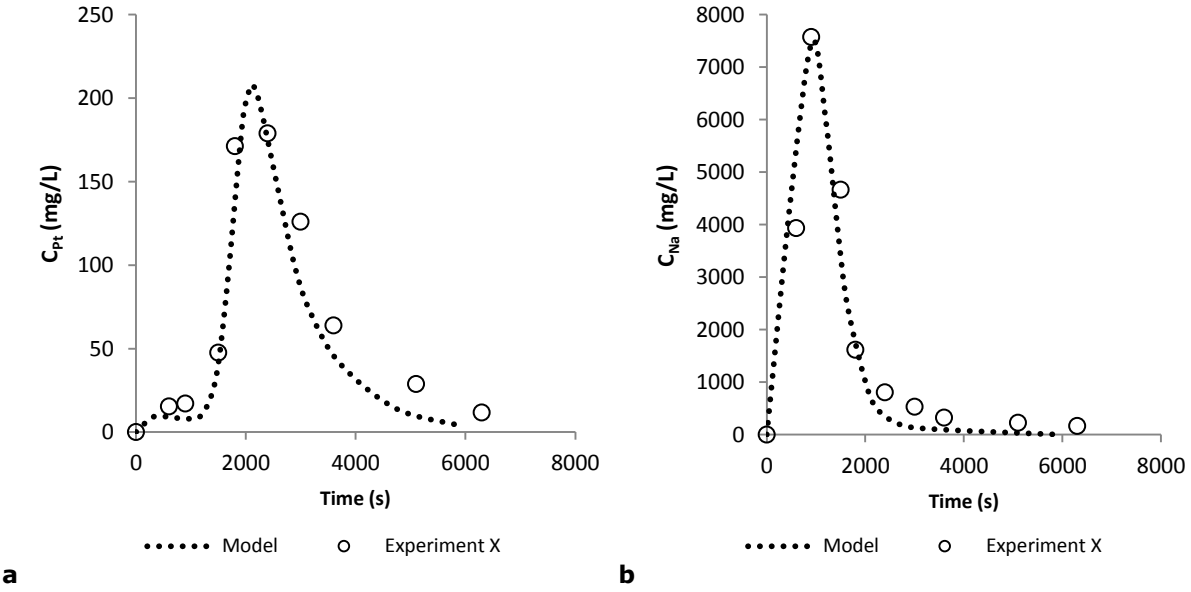


Figure 5.92: The model results compared with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 3 wt% NaCN and 1.2 wt% NaOH at 80°C.

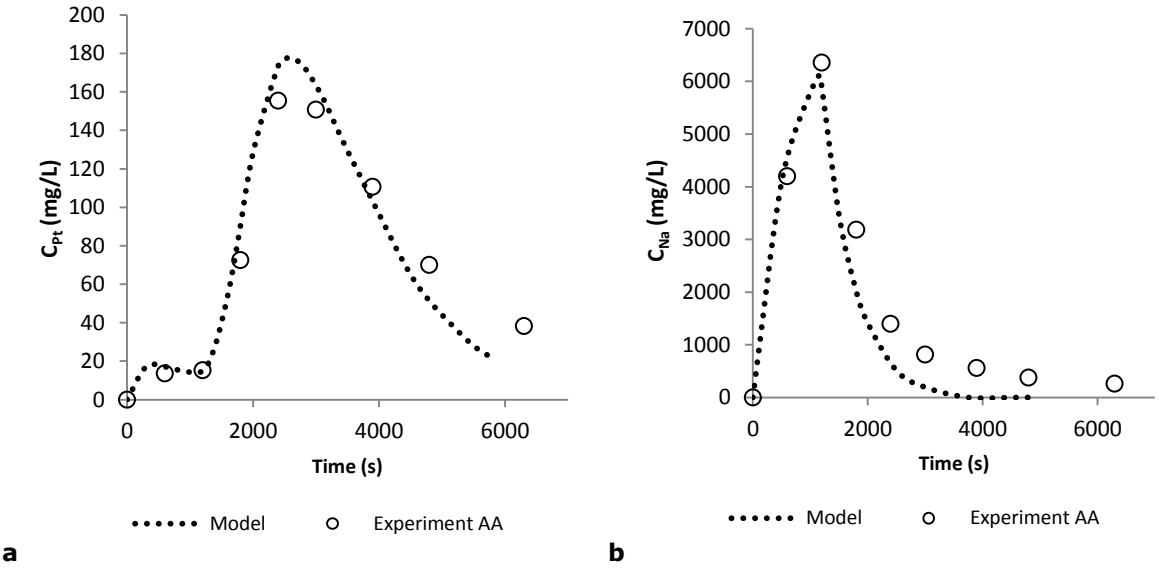


Figure 5.93: The model results compared with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 2 wt% NaCN and 1.7 wt% NaOH at 80°C.

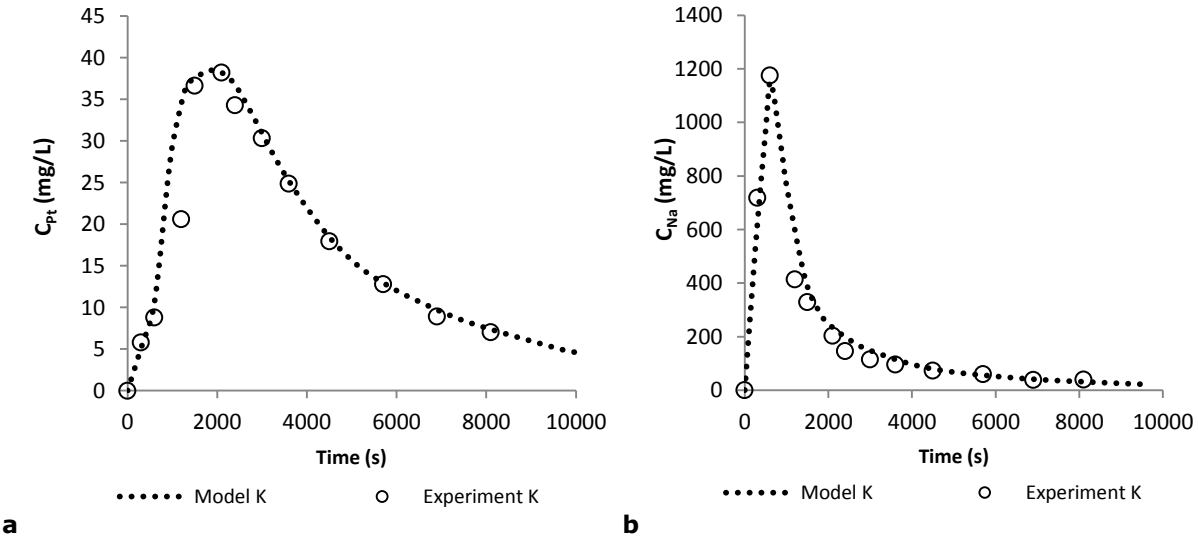


Figure 5.94: The model results with the correction factor of 0.65 compared with the elution results from experiments loaded with 650 mg/kg platinum after pre-treatment with 0 wt% NaCN and 0.6 wt% NaOH at 80°C.

5.7 Model analysis and discussion

From this developed Pt elution model, it can be concluded that the shape of the Pt elution profile for an AARL process is a function, which is mainly dependent on the removal of the Na^+ ions from the activated carbon. The height of the elution peak was found to depend on the cyanide concentration in the pre-treatment stage. This conclusion can be compared with the conclusion reached by Van Der Merwe and Van Deventer (1990), who also found that the elution of gold depends on the cation concentration in the elution column. From the derived values for the

equilibrium and film transfer constant, the Pt elution rate controlling mechanism is analysed by dividing the elution profile (Figure 5.95) into 4 time periods and discussed in combination with the decrease in Pt cyanide complexes and Na+ cations on the activated carbon as per Figure 19. Bearing in mind the dependency of the Pt elution on the Na content, as shown in Figure 5.85 and Figure 5.86, the 4 periods can be explained as follows:

Period 1. The loading of Na^+ cations on the activated carbon surface (high Q_{Na}) at the start of elution is high, resulting in a 'low' equilibrium constant B, while the Na+ cations in the bulk liquid are zero with a 'high' value for the mass transfer constant k. The Pt cyanide elution in period one is therefore predominantly equilibrium controlled.

Period 2. During period 2, the Na^+ cations are transferred from the activated carbon surface into the bulk liquid, which results in a slow increase of the equilibrium constant B, but the increasing Na^+ cations in the bulk solution now result in a low film transfer coefficient. The Pt elution during this period therefore shifts from equilibrium controlled to film transfer controlled, but as both these constants are relatively low during this period, the elution is rather slow as indicated by the horizontal slope of the Pt elution curve shown in Figure 5.96.

Period 3. The Na^+ cations on the activated carbon surface start to become entirely depleted and the concentration thereof in the bulk liquid starts decreasing as it flows out of the column. The Pt elution is now completely film transferred controlled and the rate increases dramatically with an increasing rate as the Na^+ cations are washed out of the column. This increase in the rate of elution corresponds to the observations by Adams and Nicol (1986) for Au elution results obtained from an AARL-elution in a CSTR. Adams and Nicol (1986) also attributed the increase in the elution rate to the continuous change of the ionic strength of the eluate.

Period 4. The Pt on the activated carbon surface becomes depleted and the concentration in the bulk liquid slowly decreases as the Pt flows out of the column.

The need for the addition of a cyanide factor for lower cyanide concentrations in the pre-treatment step is hypothesized to be due to the insufficient elution of the Pt, Pd and Au complexes from the activated carbon, that results in an additional amount of complexes remaining on the activated carbon surface, which leads to a lower value for the equilibrium constant B. The need for a cyanide factor to the equilibrium constant, while the film transfer constant remains unchanged, supports this hypothesis. The lower elution recovery of PGMs with less cyanide in the pre-treatment step is either due to the occurrence of more than one platinum or palladium cyanide complex on the activated carbon surface, which is influenced with the presence of free cyanide (Snyders et al., 2013) or due to a change in the functional groups on the carbon surface in the presence of cyanide, which makes the surface less receptive to adsorption (Van der Merwe and Van Deventer, 1990). In a similar fashion as when the Na^+ ions on the activated carbon surface result in a lower value for the equilibrium constant B, all complexes and ions on the activated carbon surface have this effect. The value of B is therefore further reduced by the Pt, Pd and Au ions remaining on the activated carbon when inefficient elution occurs, and ultimately leads to the different curves for the equilibrium constant B shown in Figure 5.89.

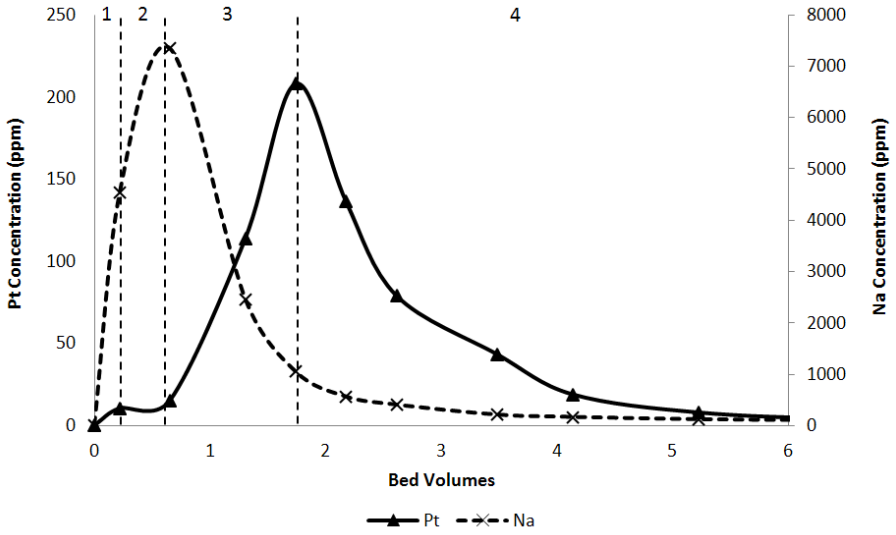


Figure 5.95: A Pt and Na elution profile at the outlet of the column divided into 4 time periods to describe the variation in the Pt elution rate.

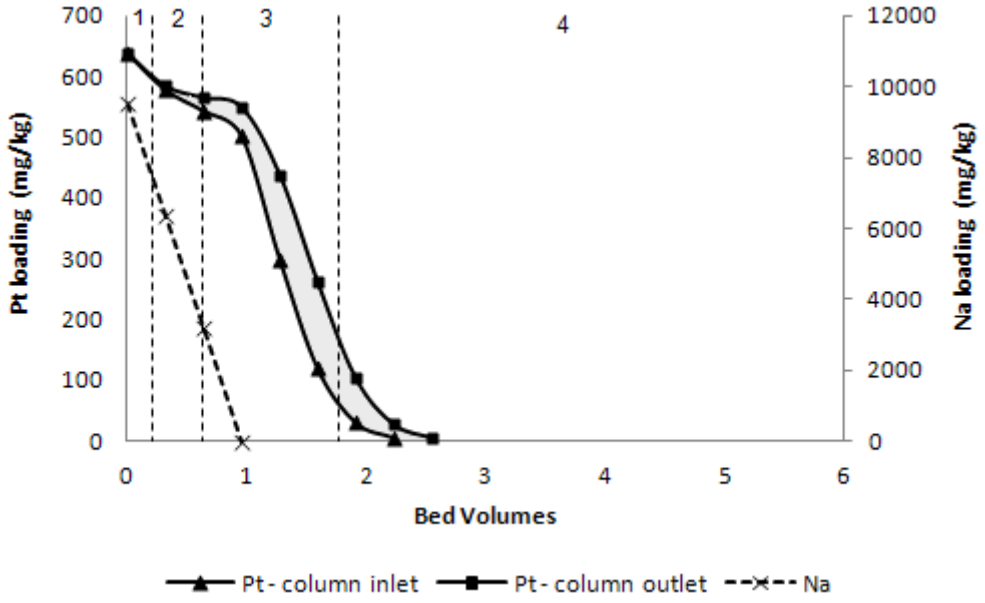


Figure 5.96: The Pt and Na loading on the activated carbon throughout the column. The loading curve is divided into 4 time periods to describe the variation in the Pt elution rate.

Continuing from Figure 5.95 and Figure 5.96, conditions through-out the column tests can now be evaluated and are shown in Figure 5.97 and Figure 5.98. The calculated mass fraction of Pt in the eluant throughout the column as the elution progresses, is shown in Figure 5.97. The coloured profiles show the variation in Pt throughout the length of the column. On the graph, the amount of Pt on the activated carbon in the centre of the column (Line AA) is compared with the mass fraction of Pt (typical elution profile) flowing out of the column with time. It is found that most of the platinum on the carbon surface is depleted halfway through the elution (3000s) and is then slowly transferred out of the column with the elution water. Stange (1991) described the AARL process as

a spatially-distributed system with changes taking place at different rates at different heights within the column. Figure 5.97 shows an example of this variability graphically with the concentration of the platinum in the water (eluant) as the elution progresses with time.

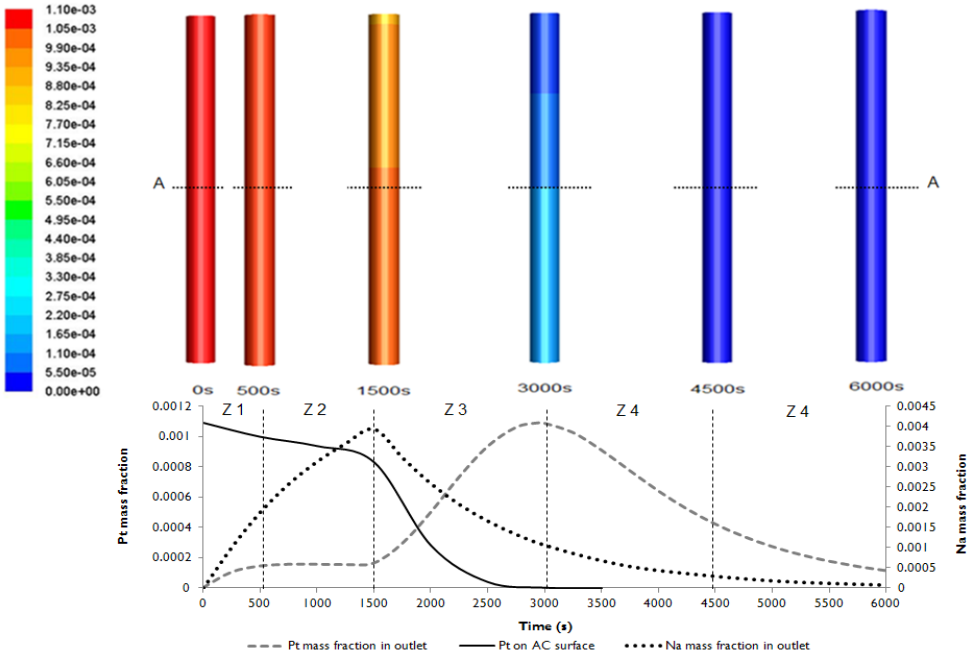


Figure 5.97: A graphical representation of the Pt mass fraction in the column as the elution progresses

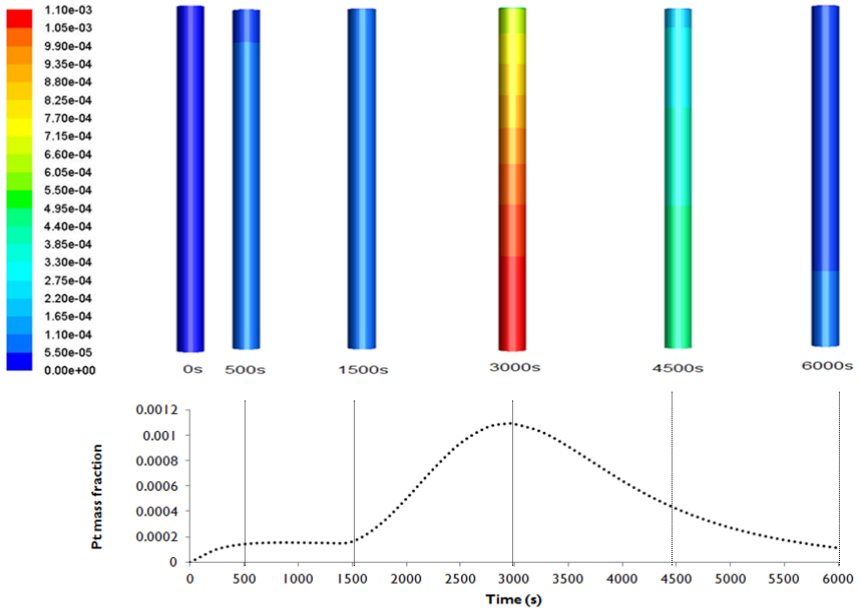


Figure 5.98: A graphical representation of the Pt concentration in the water (eluate) in the column as the elution progresses with time.

The sensitivity of the model towards the amount of Na^+ ions present is shown in Figure 5.99. The model is shown to be quite sensitive towards the presence of Na^+ ions and as these ions increase, it forces the elution recovery curve towards the right, resulting in a decrease of elution performance from 96% recovery with low Na^+ to 90% with high Na^+ at 4 bed volumes.

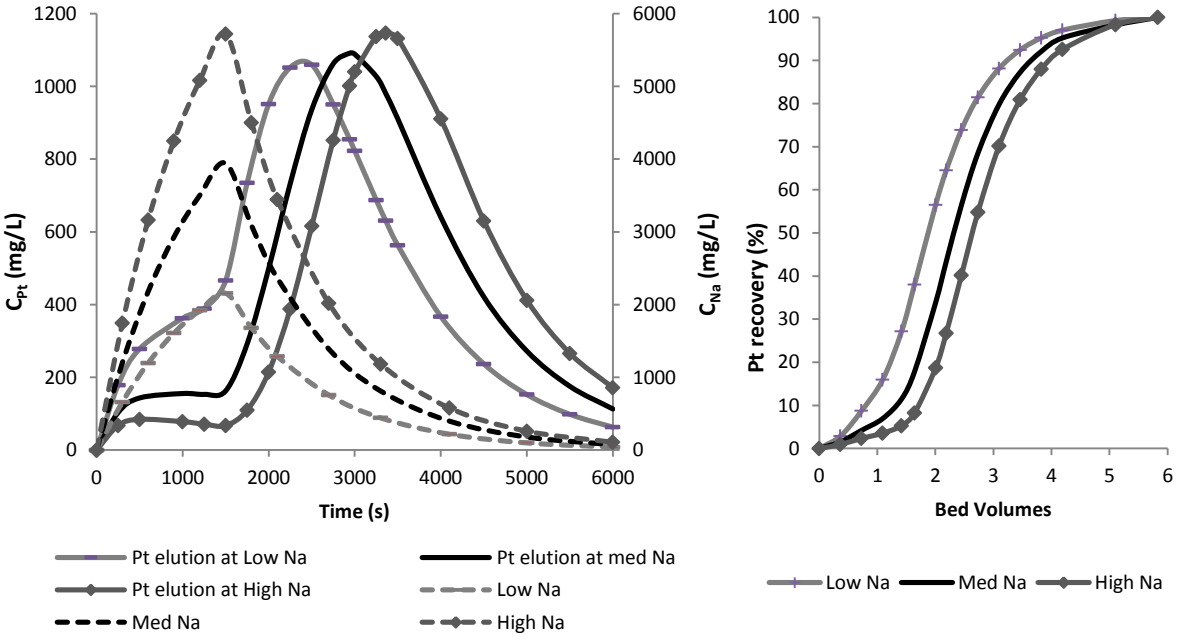


Figure 5.99: The effect of sodium ion concentration on the platinum elution performance

5.7 The effect of Na^+ ions compared to the effect of Cu

It was found in section 4.2.1.5 that the recoveries of Pt and Pd, that contained Cu and eluted at weak pre-treatment conditions (0% NaCN and 0.55% NaOH), were substantially lower (22% Pt and 32% Pd at 4 BVs) than the experiments, which did not contain copper (35 and 43% Pt, 42 and 40% Pd at 4 BVs) and therefore corresponded to the findings by Van Deventer and Liebenberg (2003) and Boshoff (1994). However, upon considering the corresponding Na^+ elution profiles (Figure 5.100) for the three recoveries curves, it could be seen that the elution profile, which showed the highest recovery, corresponded to the lowest amount of Na^{+}. The Pt and Pd recoveries where Cu was present had the highest amount of Na^+ and took the longest to elute from the column. It was therefore argued that it is the higher Na^+ ions that forced the Pt and Pd with Cu curves to the right and not due to the Cu itself. Modelling was therefore completed to determine the effect of Na+ specifically, and is shown in Figure 5.100 to Figure 5.101 below.

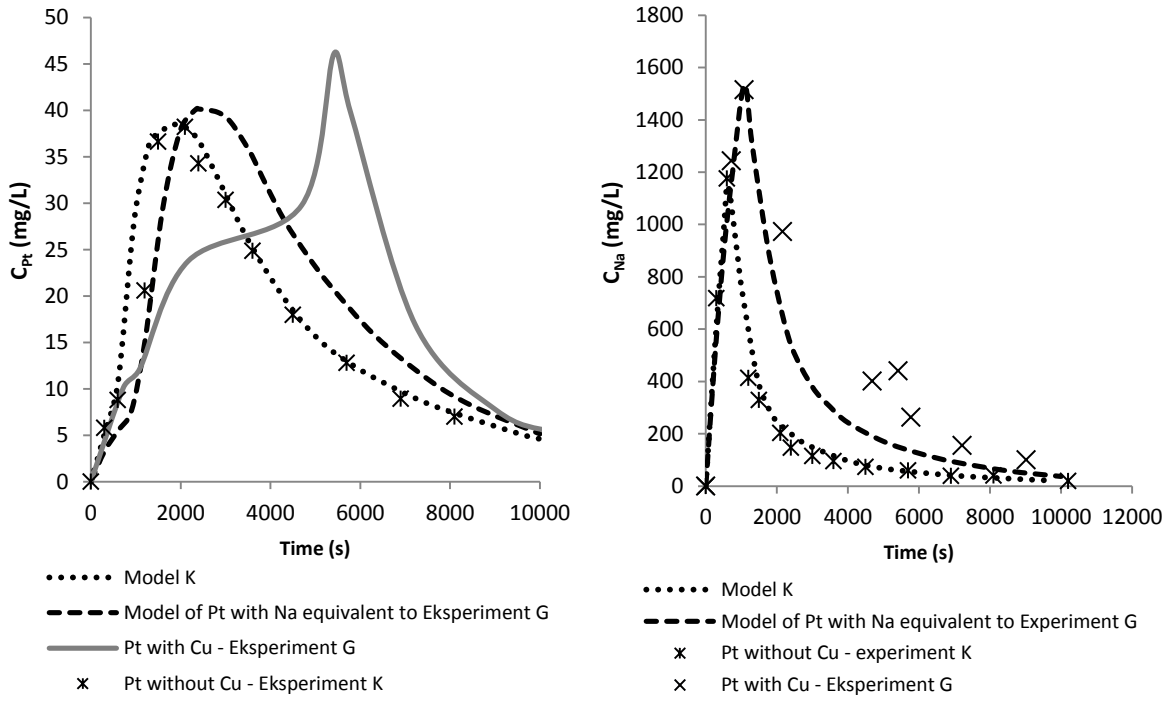


Figure 5.100: The effect of sodium ion concentration on the platinum elution performance compared to the effect of Cu at weak pre-treatment conditions (0% NaCN and 0.55% NaOH)

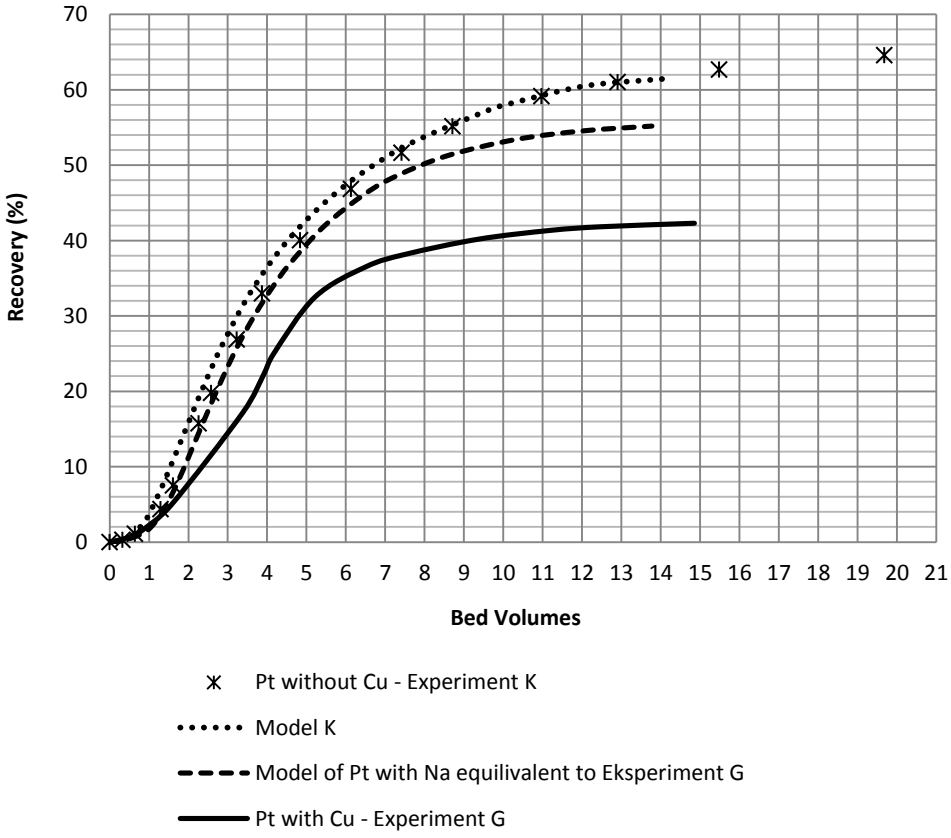


Figure 5.101: The effect of sodium ion concentration on the recovery of platinum compared to the effect of Cu at weak pre-treatment conditions (0% NaCN and 0.55% NaOH)

From Figure 5.101 it can be seen that the Pt elution curve for experiment K, which did not contain copper, had a Na^+ content equivalent to the amount of Na^+ as in experiment G (that did contain

Cu), the Pt elution curve would shift towards the right and result in a recovery decrease from 36% (Model K) to 33% at 4 BVs. The additional decrease in recovery to 23% after 4 BVs (Experiment G) is therefore attributed to the Cu locking the Pt onto the activated carbon.

5.8 The contribution of K^+ ions in the presence of SCN^-

It was considered in section 4.2.1.6 that a possible explanation to the decrease in Pt and Pd elution recovery may be due to the additional K^+ ions and not necessarily due to the presence of SCN^-. To test this possible explanation, it was calculated that the addition of the KSCN will add approximately 40 mg of K^+ ions to the system. If it is assumed that all the K^+ ions are adsorbed and eluted in a similar way to the Na^+ ions and have the same effect on the PGM elution as Na^+, (the effect will in fact be less based on the sequence of influence as discussed by McDougal (1980) and Van Deventer and Van der Merwe (1994)) the effect can be modelled and the results shows that the Pt elution decreases by 4% at 4 BV (model details shown in Figure 5.102 and Figure 5.103). The decrease in PGM elution when 100mg/L of KSCN is added, cannot therefore be explained completely by the addition of the K^+ ions. The formation of a PGM bonding with thiocyanate is therefore very likely.

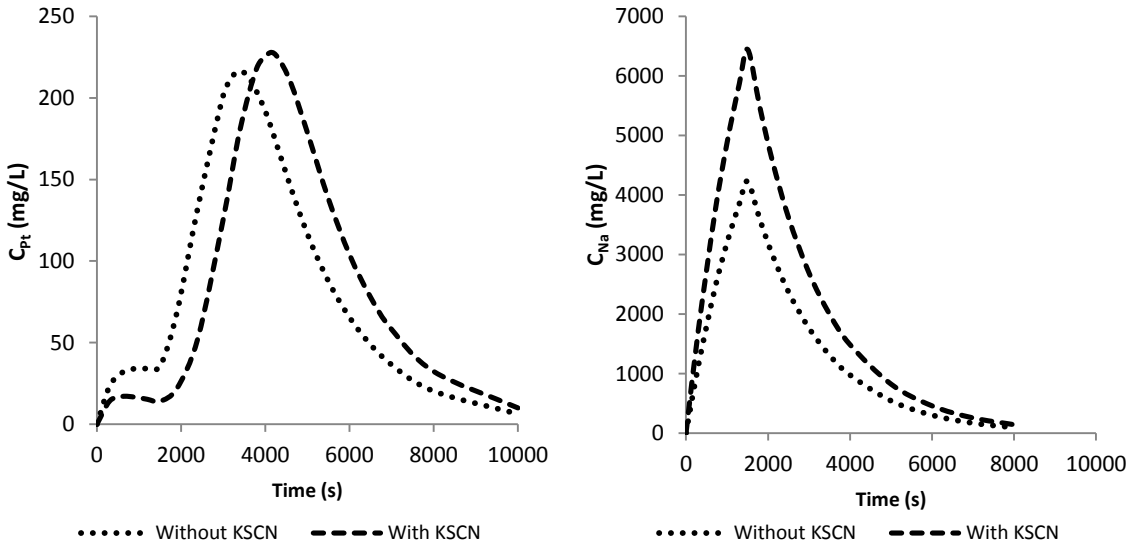


Figure 5.102: Modelling the addition of 100mg/L KSCN. The effect of the additional 40mg of K^+ ions is assumed to have a similar effect as Na^+ ions. In reality the effect will be less.

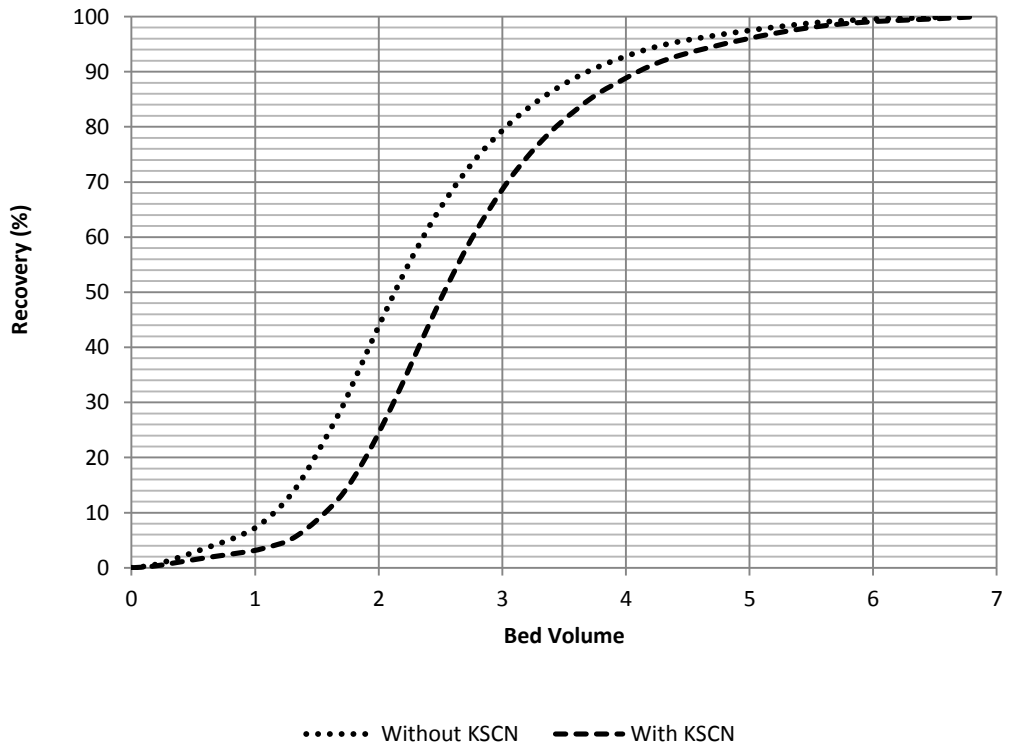


Figure 5.103: The recovery profile after modelling the addition of 100mg/L KSCN. The effect of the additional 40mg of K^+ ions is assumed to have a similar effect as Na^+ ions. In reality the effect will be less.

5.9 Conclusion on modelling

A mathematical model describing the elution of platinum cyanide in an analogue of the AARL process has been developed. The model assumes the Pt cyanide to be at an interface on the activated carbon surface where equilibrium with the liquid phase exists. From this interface the platinum then diffuses through a liquid film into the bulk of the liquid. This rate of release of the platinum complex is described by a function, which includes a modified Freundlich isotherm equation and the mass transfer diffusion equation of which the constants were found by data fitting. Both the equilibrium constant and the mass transfer constant were found to be dependent on the Na^+ ion concentration, which constantly changes with time and along the length of the column as the elution progresses.

The shape of the Pt elution profile was found to be a function, which is mainly dependent on the removal of the cations (Na^+) from the activated carbon. The model is shown to be quite sensitive towards the presence of Na^+ ions and as these ions increase, it forces the elution recovery curve towards the right, resulting in a decrease of elution performance. The height of the elution peak was also found to be dependent on the cyanide concentration in the pre-treatment stage.

Chapter 6

Conclusion

Chapter 1 of this thesis describes the need for an alternative processing option for the platinum and palladium industry, that is less energy intensive and is more able to deal with complex, lower grade ores. Leaching of platinum and palladium with cyanide has been proposed a number of times as a promising precious group metals (PGM) process option and although recoveries are problematic, progress into the understanding of cyanide leaching of PGM containing ore and concentrate has been made. Research regarding the feasibility of the subsequent upgrading and recovery of the pregnant PGM leach solution has been lacking. It is believed that a similar process to the very popular gold CIS process can be used and two of the main steps, namely the adsorption and elution onto activated carbon for platinum and palladium cyanide complexes, are investigated here.

In general it was found that the activated carbon process does seem to be a viable process consideration for the upgrading of PGMs in a cyanide leach stream. Adsorption of Pt and Pd from very dilute solutions (0.15mg/L Pt and 0.38 mg/L Pd) has been shown to be possible and the capacity of the activated carbon for Pt and Pd, as determined by single component isotherms, seems to be adequate. The elution of Pt and Pd from activated carbon with an analogue of the AARL method was found to be feasible. Pt and Pd adsorption and elution were generally found to be more sensitive to changing factors such as temperature, base metal and cyanide concentration etc. and an activated carbon recovery process for Pt and Pd cyanide will not be as robust as the gold CIS process, which is considered to be one of its main advantages.

The specific contributions made through this research project are summarized below in section 6.3.

6.1 Adsorption

Single component equilibrium isotherms were developed for Pt and Pd. To serve as a reference, the Pt and Pd isotherms were compared to gold isotherms from literature with the Pt isotherm found to be in a similar range as to that of the Au isotherms discussed. The Pd isotherm is shown to be significantly lower than the Pt isotherm at the same conditions and lower than any of the gold isotherms discussed from literature. A Freundlich isotherm was fitted to the data points of Pt and Pd with constants for A of 17068 and 9729 and n of 0.197 and 0.202 respectively.

An increase in the rate of adsorption of Pt, Pd and Au with an increase in temperature from 25 to 50°C, but a decrease in the amount adsorbed after consecutive loadings, was found with less metal adsorbing after each loading step. The presence of free cyanide was found to have a decreasing effect on the adsorption of Pt and Pd and this effect was found to increase with an increase in temperature. In all cases, Pt and Pd were found to be more sensitive to changes in conditions than Au. The low activation energies calculated for Pd, Pt and Au of 14.4, 13.9 and 11.8 kJ/mol are

indicative of a diffusion controlled process and physical adsorption rather than chemical adsorption. A higher rate of adsorption for Au than for Pt and Pd was found, while the smaller activation energy E_{act} of the Au adsorption indicates a lesser dependence on temperature.

Ni and Cu adsorption, at high and low cyanide concentrations and temperatures, was found to be vastly different from each other. Nickel adsorption was found to follow a similar trend to that of platinum and palladium adsorption with the nickel adsorption decreasing with increasing temperature and cyanide addition, and this effect increasing at both higher temperatures and cyanide addition. In general, it was found that the presence of base metals will negatively affect the adsorption of the PGMs with the adsorption of Pt and Pd being affected significantly more than the adsorption of Au. The extent to which the PGM adsorption is affected, was found to depend on the specific base metals present, the cyanide concentration as well as the temperature.

6.2 Elution

Test results showed that effective elution of Pt and Pd cyanide with the AARL method is feasible. The elution profiles for Pt and Pd were found to be steeper and to appear earlier than the elution profile of Au, indicating that Pt and Pd will elute before Au. Pt and Pd elute from activated carbon to approximately 95% in 5 BV and to >99% in 10 BVs at 80°C when pre-treated with 2% NaCN and 0.55% NaOH at room temperature.

Higher elution temperatures resulted in shift of the elution profiles towards the left, indicating better elution recoveries (≈ 64% to 99% at 4BVs) as the temperature increased from 60 to 95°C. For elution experiments performed at higher temperatures, the higher flow rate used, resulted in lower recoveries, but still indicated an increase in recovery (50 to 75 % at 4 BVs) as the elution temperature was increased from 100 to 120°C. Between 120 and 130°C, similar recoveries were recorded.

Cyanide pre-treatment has been found to have a large influence on PGM elution. The effect of the NaCN concentration shows an increase in the recovery of Pt, Pd and Au as the cyanide concentration increases from 0 to 2 %, after which the recovery starts decreasing again as the NaCN concentration increases from 2 to 4%. The occurrence of more than one platinum or palladium cyanide complex on the activated carbon surface, which is influenced with the presence of free cyanide, has been considered and deemed likely, but probably only to a fairly small degree when considering the high stability of $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$. An alternative explanation is that the presence of cyanide (and to a lesser extent NaOH), causes a change in the functional groups on the carbon surface, which makes the surface less receptive to adsorption. The NaOH was also found to affect the PGM recovery and at 0% NaCN, an increase in the recovery is seen, while at a higher cyanide concentration (2 and 3% NaCN) a decrease in the PGM recovery occurs when the NaOH concentration is increased from 0.22% to 1.65%. The increase is related to the increase in the solution pH, which will favour desorption, and the decrease in recovery for higher NaCN and NaOH concentrations is ascribed to the increase in the ionic strength.

The effect of increasing ionic strength of the elution water, represented by an increase in Na^+ cations on the elution recovery of Pt and Pd, was investigated. A general decrease in Pt, Pd and Au

recovery is seen as the ionic strength of the elution water increases and is consistent with literature.

The effect of hydrochloric acid treatment on the elution of Pt and Pd was investigated. For all the cases, the Pt and Pd recovery increased when an acid pre-treatment was performed, compared to no acid pre-treatment. In none of the cases did any of the Pt, Pd or Au elute with the acid or the following rinsing water at 25°C. No Cu and Ni were eluted with cold acid and a marginal 1.3 to 3% of the Cu with hot acid. A significant 64 to 75% of the Ni, however, eluted with the hot acid pre-treatment. Following the hot acid pre-treatment an additional 9.1 to 10.5 % Ni was eluted with the rinsing water. It is also interesting to note that the lowest recovery of copper occurs when the acid concentration is high (3M) and hot (70°C). This is hypothesized to be due to the increased formation of either CuCN or $[Cu(CN)_2]^{-}$, which requires a more concentrated or simply a longer cyanide pre-treatment step to convert the copper cyanide complexes to $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ which readily elutes with hot de-ionized water.

The elution recovery of Pt and Pd from a carbon loaded to equilibrium shows a shift in recovery towards the right indicating slower recovery with the higher loaded activated carbon. This change in elution kinetics of Pt and Pd with the carbon loading is therefore explained by the proximity of the loading on the activated carbon to its surface saturated values. With surface saturation reached, the PGMs will start diffusing into activated carbon particles, which occur at a slower rate and will therefore desorb at a slower rate as well. The slower diffusion of the PGMs out of the macro and micro pores will therefore cause the peak to shift towards the right of the graph as found here.

In the presence of copper cyanide, the elution order has been found to be copper, platinum and palladium simultaneously and gold eluting last. The cyanide pre-treatment has also been found to have a major influence on the elution of Cu and can be explained by the difference in the absorbance strength between the different copper cyanide complexes. The presence of Cu did not have a negative effect on the elution of Pt, Pd or Au at strong pre-treatment (2% NaCN and 0.55% NaOH) conditions as similar recovery curves with and without Cu were found. At weak pre-treatment conditions, the recovery of Pt and Pd was reduced by between 10 and 18% after 5 BVs when Cu was present.

The presence of 100 mg/L KSCN salt added to the leach solution during the adsorption stage, reduced the elution recovery of the PGMs at 5 bed volumes from 95% for Pt and Pd when not present to approximately 88% for Pd and 85% for Pt when present. A possible explanation may be due to additional K^+ ions and not necessarily due to the presence of SCN^-.

A maximum amount of 0.15% for Pt, 0.28% Pd and 0.6% Au was found to report to the pre-treatment solution. For the higher loading on the activated carbon, which is expected to be a better representation of plant conditions, 0.07% Pt, 0.11% Pd and 0.12% Au reported to the pre-treatment solution. No correlation between the pre-treatment NaCN or NaOH concentration and the PGM concentration could be determined, and it is therefore concluded that these concentrations have no effect on the amount of PGMs that are desorbed during the pre-treatment step. The PGM concentration in the pre-treatment solution is attributed to the distribution of the PGMs on the

carbon particle and even though very small, a certain amount of these PGMs would readily desorb or wash off the carbon.

A mathematical model describing the elution of platinum cyanide in an analogue of the AARL process has been developed. The model assumes the Pt cyanide to be at an interface on the activated carbon surface where equilibrium with the liquid phase exists. From this interface the platinum then diffuses through a liquid film into the bulk of the liquid. This rate of release of the platinum complex is described by a function, which includes a modified Freundlich isotherm equation and the mass transfer diffusion equation of which the constants were found by data fitting. Both the equilibrium constant and the mass transfer constant were found to be dependent on the Na^+ ion concentration, which constantly changes with time and along the length of the column as the elution progresses.

The shape of the Pt elution profile was found to be dependent on the removal of the cations (Na^+) from the activated carbon. The model is shown to be quite sensitive towards the presence of Na^+ ions and as these ions increase, it forces the elution recovery curve towards the right resulting in a decrease of elution performance. The height of the elution peak was also found to be dependent on the cyanide concentration in the pre-treatment stage.

6.3 Practical implications

Some of the major advantages of gold CIP plants are that they are mechanically robust, handle plant upsets remarkably well and are highly tolerant to changes in feed composition (Fleming et al. 2011). This is also evident from the Au adsorption curves presented here, which were significantly less affected by changes in the temperature, cyanide and impurity content, which is primarily related to the high selectivity of activated carbon towards the aurocyanide complex. While it has been indicated that single component isotherms were found to be in a similar range to some Au adsorption isotherms, Pt and Pd adsorption is significantly more affected by the stream composition. While the slower adsorption of Pt and Pd can be compensated for by a detailed plant design, the higher sensitivity will require tight operational control, as plant upsets and changes in the feed composition may lead to significant PGM losses. High temperature leaching will require a cool down period to temperatures where adequate adsorption can take place. The sensitivity of Pt and Pd adsorption to the presence and co-adsorption of base metals is problematic and dictates the necessity for a pre-removal step such as the SART process (Botz et al. 2011).

The elution of Pt and Pd from activated carbon with an analogue of the AARL method was found to be feasible and the elution process is expected to closely resemble a typical gold elution process. While an economic trade-off study will have to be completed to verify the operating conditions, that will result in the highest investment return, it is expected that the process will most likely be operated at pre-treatment concentrations of 2.5% NaCN and 0.6% NaOH at room temperature, while the elution step will occur at 120°C with 4 BVs of de-ionised water. For high Au concentrations on the carbon, a shift towards higher cyanide concentrations in the pre-treatment step and more BVs of eluant will have to be considered. A HCl wash prior to elution is expected to result in higher PGM recoveries.

6.4 Specific contribution made

The thesis set out to establish the feasibility of a carbon adsorption and elution process for the upgrading of Pt and Pd cyanide complexes and is the first comprehensive study in this regard. Where none existed, single component Pt- and Pd- cyanide activated carbon adsorption isotherms were determined and compared to Au isotherms from literature. When the effects of operating conditions such as temperature, cyanide concentrations and carbon activity together with stream impurities such as base metals are considered, no information could be found in the open literature. These conditions were investigated at dilution ranges as found in heap leaching, and the effects are now established.

Prior to this study, the stripping/elution of Pt and Pd from activated carbon remained a question mark for which a solution has been provided here. Without a suitable elution method, the use of activated carbon in a Pt and Pd process would have been unlikely, and therefore the investigation here paves the way for this technology. In addition, factors affecting this process have been investigated, which will enable the determination of suitable operating conditions for a given process. Mathematical modelling of Pt elution from activated carbon has been completed with kinetic parameters determined by fitting the models to experimental results. A novel step wise mechanism of elution is discussed.

Chapter 7

Recommendations

For the continuous development of the process, several additional studies need to be undertaken.

7.1 Adsorption

By comparing the Pt and Pd isotherms to Au isotherms found in literature and considering the potential of activated carbon to adsorb Pt and Pd from very diluted solutions (0.15mg/L Pt and 0.38 mg/L Pd), activated carbon does indeed seem to be a viable process consideration for the upgrading of PGMs in a cyanide leach stream. Before a definite conclusion can be made, however, pilot scale experiments are recommended to determine the upgrade ratio and carbon adsorption capacity at plant conditions. Pilot scale experiments will also assist in the design and sizing of the adsorption stages of a CIS plant for Pt and Pd.

7.2 Elution

No work has been published on the reaction kinetics of the cyanide pre-treatment for Pt and Pd and neither for Au. The reaction kinetics can be researched by studying the influence of the pre-treatment variables such as the stirring, temperature and residence time on the elution of the Pt, Pd and Au in the subsequent elution step. Understanding the reaction kinetics in the pre-treatment step can lead to reduced industrial gold elution costs and may provide additional insight into the elution mechanism.

It has been found that an acid wash pre-treatment increases the recovery of Pt and Pd after approximately 5 BVs. Very little, however, is known about the mechanism that occurs to increase the Pt and Pd recovery. It is also unknown whether the optimum NaCN pre-treatment concentration of approximately 2.5% found during this study is still applicable and whether this cyanide concentration will be different after an acid pre-treatment step.

Only the effect of Na was considered on the elution process. The effect of the other cations needs to be investigated as well.

The adsorption and elution of Pt and Pd has been investigated with activated carbon originating from a single batch and supplier. There is no reason to believe that activated carbon from an alternative source will have a dramatic different result, but it may result in a shift in recovery and different pre-treatment requirements, which need to be verified.

Modelling of the Pt elution has been completed and validated against laboratory elution experiments. No known model for the elution of platinum or palladium or even gold, for which the

AARL process was developed for, exists and the further development of the current model into a suitable predictive model may therefore lead to several optimisation possibilities. The following work is recommended:

- The model does not incorporate Pd, Au and additional cations. As these metals may affect each other, these data need to be known for accurate elution modelling.
- The elution of the Pt has been found to depend largely on the elution of Na^+. Very little information is available on the rate and what affects the Na^+ elution from activated carbon and is critical in the development of an elution model.
- Temperature has been shown to affect the PGM elution significantly. Incorporation of the temperature effects into the model and temperature effects in large scale elution columns need to occur.
- The model needs to be expanded to include gold for which large scale industrial data are available for validation.

References

1. Adams, M.D., 1990. The mechanism of adsorption of aurocyanide onto activated carbon I. Relation between the effects of oxygen and ionic strength. Hydrometallurgy, 25, 171.
2. Adams, M.D., 1991. Chemistry of adsorption and elution of gold on activated carbon, Recent developments in In-Pulp technology, The south African Institute of mining and metallurgy, 7 – 8 October 1991. ISBN 1-874832-12-9
3. Adams, M.D., 1992. The mechanism of adsorption of $Ag(CN)_2^-$ and Ag^+ on to activated carbon. Hydrometallurgy, 31, pp 121 – 138.
4. Adams, M.D., Fleming, C.A., 1989. The mechanism of adsorption of aurocyanide onto activated carbon. Metallurgical Transactions B. Vol 20B. June. pp 315 – 325.
5. Adams, M.D., Friedl, J, Wagner, F.E., 1995. The mechanism of adsorption of aurocyanide on to activated carbon, 2. Thermal stability of the adsorbed species, Hydrometallurgy 37, pp 33-45.
6. Adams, M.D, Friedl, J, Wagner, F.E, Adams, M.D, Friedl, J, Wagner, F.E, 1992. The mechanism of adsorption of $Au(CN)_4^-$ onto activated carbon. Hydrometallurgy, 31, pp 265-275.
7. Adams, M.D., Lawrence, R., Bratty, M., 2008. Biogenic sulphide for cyanide recycle and copper recovery in gold–copper ore processing, Minerals Engineering 21, pp 509–517.
8. Adams, M.D., McDougal, G.J., Hancock, R.D., 1987. Models for the adsorption of aurocyanide onto activated carbon. Part 3: Comparison between extraction of aurocyanide by activated carbon, polymeric adsorbants and 1-Pentanol. Hydrometallurgy vol 19, pp 95 – 115.
9. Aguilar, M., Farran, A., Marti, V., 1997. Capillary electrophoretic determination of cyanide leaching solutions from automobile catalytic converters, Journal of Chromatography A, 778, pp 397-402.
10. Al-Ghouti, M., Khraisheh, M.A.M., Ahmad, M.N.M., Allen, S., 2005. Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study. Journal of Colloid and Interface Science 287 (2005) pp 6 – 13.
11. Allard, L.F., Borisevich, A., Deng, W., Si, R., Flytzani-Stephanopoulos, M., Overbury, S.H., Evolution of gold structure during thermal treatment of Au/FeO_x catalysts revealed by aberration-corrected electron microscopy, Journal of Electron Microscopy 58(3), pp 199–212.
12. Aso, H., Matsuoka, K., Sharma, A., Timita, A., 2004. Structural analysis of PVC and PFA carbons prepared at 500–1000 °C based on elemental composition, XRD, and HRTEM. Carbon 42, pp 2963–2973.
13. Atkins, P, de Paula, J, 2006. Physical Chemistry – 8th edition. Oxford University press. pp 877.
14. Aylmore, M.G, Alternative lixiviants to cyanide for leaching gold ores. Developments in Mineral Processing, (15):501-539.
15. Bahta, A, Parker, G.A, Tuck, D.G, 1997. Critical survey of stability constants of complexes of thiocyanate ion, Pure and Applied Chemistry, Vol 69, No 7, pp 1489 – 1548.
16. Baştuğ, T, and Kuyucak, S, 2005. Temperature dependence of the transport coefficients of ions from molecular dynamics simulations, Chemical Physics Letters, 408, pp 84–88.
17. Baur, J.E., and Wightman, R.M., 1990. Diffusion coefficients determined with microelectrodes, J . ElectroanaL Chem., 305, pp 73-81.
18. Boshoff, P.T.E, Cyanide-free AARL elutions are feasible, Minerals Engineering, vol 7, Nos 2/3, pp 251 – 264, 1994
19. Botz, M., Kaczmarek, A., Orser, S., 2011. Managing Copper in leach solution at the copper gold project: Laboratory testing and process design. Minerals & Metallurgical Processing, 2011, Vol. 28, No. 3, pp 133 -138.
20. Bruneau, C.H., Mortazavi, I., 2008. Numerical modelling and passive flow control using porous media. Computers & Fluids, 37, pp 488 – 498.

21. Chen, J, Huang, K, A new technique for extraction of platinum group metals by pressure cyanidation. Hydrometallurgy 82 (2006) 164–171
22. Chen, S., Xu, R., Huang, H., Yi, F. Zhou, X. & Zeng, H. Reduction-adsorption behavior of platinum ions on activated carbon fibers. Journal of Materials Science, 42:9572-9581, 2007
23. Chidyagwai, P, Rivière, B, 2009. On the solution of the coupled Navier-Stokes and Darcy equations. Comput. Methods. Appl. Mech. Engrg. 198 pp 3806 – 3820.
24. Cho, E., Dixon, S., Pitt, C., 1979. The kinetics of gold cyanide adsorption onto activated carbon. Met. Trans. B. Vol 10, Issue 2, pp 185 – 189
25. Cimolin, F, Discacciati,M, 2013. Navier Stokes/Forchheimer models for filtration through porous media. Applied Numerical Mathematics. APNUM 2735, In press.
26. Clark, J.H., Duke, C.V.A., Brown, S.J., Miller, J.M., 1986. Infrared spectroscopic studies on metal cyanides adsorbed on inorganic support materials. Spectrochemica Acta, Vol 42A, No 7, Pp 811 – 814.
27. Cook. R., Crathorne, E.A., Monhemius, A.J., Perry, D.L., 1989. An XPS Study of the adsorption of gold(I) Cyanide by Carbons. Hydrometallurgy, 22 (1989) pp 171 – 182.
28. Cook. R., Crathorne, E.A., Monhemius, A.J., Perry, D.L., 1989. An XPS Study of the adsorption of gold(I) Cyanide by Carbons -reply. Hydrometallurgy, 25 (1990) pp 387 – 396.
29. Cortina, J., Meinhardt, E., Roijals, O., Marti, V., 1998. Modification and preparation of polymeric adsorbents for precious-metal extraction in hydrometallurgical processes. Reactive and Functional Polymers, vol. 36, pp. 149 -165.
30. Costello, M.C., McLean, E., Burdett, B., 1988. Carbon adsorption, elution and electrowinning of gold ores with up to 4:1 silver to gold ratios. In: Randol Gold Conference 1988, Perth. Randol International, Golden, Colorado.
31. Cramer, L.A., 2001. The Extractive Metallurgy of South Africa's Platinum Ores, JOM, October.
32. Dai, X., Jeffrey, M.I., Breur, P.L., 2010. A mechanistic model of the equilibrium adsorption of copper cyanide species onto activated carbon. Hydrometallurgy 101 (2010) pp 99 – 107.
33. Davidson, R.J, A review of the *AARL* process for the elution of gold from activated carbon, Lecture 15, *C.LP. School,* S. Afr. Inst. Min. Metall., Johannesburg, South Africa, 23 (1986).
34. Davidson, R.J, The mechanism of gold adsorption on activated charcoal, *J. S.Afr. Inst. Min. Metall.,* 75(4), 67-76 (1974).
35. Davidson, R.J, Baily, P.R, Carbon Elution, The south African Institute of mining and metallurgy, 7 – 8 October 1991
36. Davidson, R.J, Duncanson, D. The elution of gold from activated carbon using deionized water, Journal of the South Africa institute of mining and metallurgy, July 1977, pp 254 -261
37. Davidson R.J, Douglas W.D. and Tumilty J.A. Aspects of laboratory and pilot plant evaluation of CIP with relation to gold recovery. CIM XIV International Mineral Processing Congress. Toronto, Canada, (1982)
38. Davidson, R.J. and Veronese, V., 1979. Further studies on the elution of gold from activated carbon using water as the eluant. J. S. Afr. Inst. Min. Metall., 1979, vol 79, pp 437 – 445.
39. Davidson, R.J., Veronese, V. and Nkosi, M.V. 1979. The use of activated carbon for the recovery of gold and silver from gold-plant solutions. Journal of the Southern African Institute of Mining and Metallurgy, May 1979.
40. De Haas, K.S., Fouche, C.M., Fouché, K.F., 1977. The chemistry of some group VIII metals in molten cyanide, Part 1. Ru, Os, Rh and Ir. Inorganica Chimica Acta, 21 (1977) 15-22
41. De Haas, K.S, Fouché, K.F., 1977. The chemistry of some group VIII metals in molten cyanide, Part 2. Ni, Pd, Pt. Inorganica Chimica Acta, 24 (1977) 269-276
42. Desmond, D.P, Atkinson, G.B, Kuczynski, R.J,Walters, L.A, High-temperature cyanide leaching of platinum-group metals from automobile catalysts – laboratory tests, Report of investigations 9384, 1991

43. Dionex Corporation, 2003. Direct Determination of Metal Cyanides by Ion Chromatography with UV Absorbance Detection, Application Update 147, LPN 1570 PDF 1/04, 2003
44. Dudukovic, M.P., and Felder, 2012. R.M., Mixing effects in chemical reactors 3, Dispersion model. Sekharbhatta, Modular Instruction Series, American Institute of chemical engineers. Module E4.6
45. Eksteen,J.J, Mwase, J.M, Petersen, J, Bradshaw, S.M, Akdogan, G, Mpinga, N, Snyders, C.A, A novel energy efficient process for the extraction of platinum group metals through a sequential staqge high temperature heap leach process and subsequent recovery and elution using activated carbon, Biohydrometallurgy 2012, Falmouth, Cornwall, UK, 18 -20 June 2012
46. Fleming, C.A, Mezei, A, Bourricaudy,E, Canizares, M, Ashbury, M, Factors influencing the rate of gold cyanide leaching and adsorption, and their impact on the design of CIL and CIP circuits, Minerals Engineering, Vol. 24, No. 6, 2011
47. Fleming, C.A and Nicol, M.J., 1984. The adsorption of gold cyanide into activated carbon III: Factors influencing the rate of loading and capacity. J. S. Afr. Inst. Min. Metall., vol. 84, no. 4. Apr. 1984. pp. 85-93.
48. Fluent 12.0, 2009. Theory Guide
49. Ford, K.J.R., Henderson, R.D., Fleming, C.A., 2008. Application of the SART process to heap leaching of gold copper ores at Maricunga, Chile, SGS Mineral Services, Technical Bulletin 2008 – 51.
50. Fisher M.J., LaBrooy S.R., 1997. The effect of nickel on gold recovery during adsorption and elution, World Gold 97 Conference, Singapore, 1- 3 September, pp 99 - 107
51. Fritz, W., Schlunder, E., 1974. Simultaneous adsorption equilibria of organic solutes on activated carbon, Chemical Engineering Science, 29, 1279 – 1282
52. Fuerstenau, M.C., Nebo, C.O., Kelso, J.R., Zaragoza M, R., 1987. Rate of adsorption of gold cyanide on activated charcoal. Minerals and Metallurgical processing. November 1987.
53. Furukawa, K, and Takahashi, Y, 2008. Effect of complexation with humic substances on diffusion of metal ions in water, Chemosphere, 73, pp 1272–1278.
54. Gallagher, N.P., Hendrix, J.L., Milosavljevic, E.B., Nelson, J.H., Solujic, L., 1990. Affinity of activated carbon towards some gold(I) complexes, Hydrometallurgy, 25, pp 305-316
55. Grimsley, W.D., 1991. Regeneration and acid washing practise, Recent developments in in-pulp technology, The South African Institute of Mining and Metallurgy, ISBN 1-874832-12-9, 7-8 Oct.
56. Grunwald, P, 1989. Determination of Effective Diffusion Coefficients - an Important Parameter for the Efficiency of Immobilized Biocatalysts. Biochemical education, 17(2), pp 99 – 102.
57. Hamáček, J., Havel, J., 1999. Determination of platinum(II,IV) and palladium(II) as thiocyanate complexes by capillary zone electrophoresis: Analysis of carboplatin and similar drugs. Journal of chromatography A, Vol 84, Issues 1 – 2, February 1999, pp 321 - 327.
58. Hancock, R.D., Evers, A., 1976. Formation constant of $Pd(CN)_4^{2-}$, Inorganic Chemistry, Vol. 15, No. 4, pp 995 – 996
59. Hancock, R.D., Finkelstein, N.P., Evers, A., 1977. A linear free-energy relation involving the formation constants of palladium(II) and platinum (II), J. Inorg. Nucl. Chem., Vol. 39, pp 1031-103
60. Hancock, R.D, Finkelstein, N.P, Evers, A, 1972. Stabilities of the cyanide complexes of the monovalent group IB metal ions in aqueous solutions. J. Inorg. Nucl. Chem., 1972, Vol. 34, pp. 3747 – 3751.
61. Heinen, H.J., Peterson, D.G., Lindstrom, R.E., 1978. Processing Gold ores using heap leach-carbon adsorption methods, Bureau of Mines Information Circular 8770.
62. Hibble, S.J., Chippendale, A.M., Bilbe, E.J., Marelli, E., Harris, P.J.F., Hannon, A.C., 2011. Structures of $Pd(CN)_2$ and $Pt(CN)_2$: Intrinsically Nanocrystalline materials? Inorg. Chem. 2011, 50, 104–113
63. JCGM 100, 2008. Evaluation of measurement data – guide to the expression of uncertainty in measurement, First edition, September, 2008.
64. Jeffrey, M., Pleysier, R., Bunney, K., 2009. Elution behaviour of metals from carbon, Hydrometallurgy conference 2009, The Souther African Institute of Mining and Metallurgy.

65. Jia, Y.F., Steele, C.J., Hayward, I.P., Thomas, K.M., 1998. Mechanism of adsorption of gold and silver species on activated carbons. Carbon. Vol 36, No 9. pp 1299 – 1308.
66. Jones, W.G., Klauber, C., Linge, H.G., 1989. Fundamental aspects of gold cyanide adsorption on activated carbon. Gold Forum on technology and practices – World Gold 89, Reno, NV, USA, 5 Nov 1989; Code 12880
67. Kappes, D.W., 2002. Precious metal heap leach design and practise. Mineral Processing Plant Design, Practice and Control, Volume 1, SME (1606).
68. Kononova, O.N, Kholmogorov, A.G, Danilenko, N.V, Goryaeva, N.G., 2007. Recovery of silver from thiosulfate and thiocyanate leach solutions by adsorption on anion exchange resins and activated carbon, Hydrometallurgy 88 (2007) 189–195
69. Kuczynski, R.J., Atkinson, G.B., Walters, L.A., 1992. High-temperature cyanide leaching of platinum-group metals from automobile catalysts-process development unit, Report of investigations 9428.
70. Ladeira, A.C.Q., Figueira, M.E.M., Chiminelli, V.S.T., 1993. Characterization of activated carbons utilized in the gold industry: Physical and chemical properties and kinetic study. Minerals Engineering, Vol 6, No 6, pp 585 – 596.
71. Laxen, P.A., 1984. Carbon in Pulp processes in South Africa, Hydrometallurgy, 13 (1984) 169-192
72. Lee, J.W., Yang, T.H., Shim, W.G., Kwon, T.O., Moon, I.S., 2007. Equilibria and dynamics of liquid-phase trinitrotoluene adsorption on granular activated carbon. Journal of Hazardous Materials 141. Pp 185 – 192.
73. Lewins, J.D., 2003. The "Panton Process" successful on South African platinum concentrates. MEI Online, 15 November. http://www.min-eng.com/hydrometallurgy/52.html
74. Liddell, K.S. and Adams, M.D. 2012, Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates, Journal of the Southern African Institute of Mining and Metallurgy, vol. 112, no. 1. pp. 31 – 36.
75. Liebenberg, S.P., van Deventer, J.S.J., 1997. The dynamic simulation of in-pulp sorption processes using the lumping of competitive and fouling phenomena. Minerals Engineering 10 (9).
76. Lorenzen, L, Van Deventer, J.S.J., 1992. The mechanism of leaching gold from refractory ores, Minerals Engineering, Vol. 5, Nos 10-12, pp. 1377-1387
77. Lu, J, Dreisinger, D.B, Cooper, W.C., 2002. Thermodynamics of the aqueous copper-cyanide system, Hydrometallurgy 66 (2002) 23–36
78. Lunga, A.L., 2006. Optimizing the operating conditions of gold elution and electrowinning for Tau Lekoa stream at Kopanang gold plant. M.Sc thesis, University of the Witwatersrand.
79. Marsh, H., Rodríquez-Reinoso, F., 2006. Chapter 7 – SEM and TEM images of structures in Activated Carbons. Activated Carbon. Elsevier, ISBN: 0080444636, pp 366 – 382.
80. Marinovic, V, Ristic, M, Dostanic, M, 2005. Dynamic adsorption of trinitrotoluene on granular activated carbon. Journal of Hazardous Materials B117, pp 121 – 128.
81. Marsden, J. O. & House, C. I., 2006. The Chemistry of Gold Extraction (Second Edition). 2006. Littleton, CO: Society for Mining, Metallurgy and Exploration, Inc., Littleton, Colorado.
82. McDougal, G.J., 1991. The physical nature and manufacture of activated carbon, J.S. Afr. Inst. Min. Metall., vol 91, no.4. April 1991, pp 109 – 120
83. McDougall, G.J., Hancock, R.D., Nicol, M.J., Wellington, O.L. & Copperthwaite, R.G. 1980. The Mechanism of the adsorption of gold cyanide on activated carbon. Journal of South African Institute of Mining and Metallurgy, 80:344-356.
84. McInnes, C.M., Sparrow, G. J and Woodcock, J.T. 1994. Extraction of platinum, palladium and gold by cyanidation of Coronation Hill ore. Hydrometallurgy, vol. 35. pp. 141 – 159.
85. Meng, X, Han, K.N., 1993. Adsorption of gold from iodide solution onto activated carbon. SME Annual Meeting, Reno, Nevada – February 15 – 18, 1993.

86. Milbourne, J, Tomlinson, M, Gormely, L, Use of hydrometallurgy in direct processing of base metal/PGM concentrates, Hydrometallurgy 2003 – Fifth International Conference in Honor of Professor Ian Ritchie – Volume 1: Leaching and Solution Purification, TMS (The minerals, metals and materials society), 2003
87. Millard, M, Processing of high-silver gold ores, Chapter 34, Developments in Mineral Processing, Vol. 15, Mike D. Adams (Editor), Elsevier B.V, 2005, pp 849 - 859
88. Monlien, F.,J., Helm, L, Abou-Hamdan, A, Merbach, A. E., 2002. Mechanistic Diversity Covering 15 Orders of Magnitude in Rates: Cyanide Exchange on $[M(CN)_4]^{2-}$ (M = Ni, Pd and Pt)[1], Inorganic chemistry 2002, 41, 1717 - 1727
89. Mpinga, C.N, 2012, The extraction of precious metals from an alkaline cyanided medium by granular activated carbon, MSc thesis, University of Stellenbosch, Nov 2012
90. Mpinga, C.N, Bradshaw, S.M, Akdogan, G, Snyders, C.A, 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. Hydrometallurgy 142, pp 36 – 46.
91. Mwase, J.M, 2009. Hydrometallurgical extraction of platinum group metals from a low grade ore concentrate, MSc thesis, University of Capetown, October 2009
92. Mwase, J.M., Peterson, J, Eksteen, J.J., 2012. A conceptual flow sheet for heap leaching of platinum group metals (PGMs) from low-grade concentrate, Hydrometallurgy 111-112 (2012) 129–135
93. Mwase, J.M., Peterson, J., Eksteen, J.J., 2014. A novel sequential heap leach process for treating crushed Platreef ore. Hydrometallurgy, Vol. 141, January, pp 97-104.
94. Nicol, M.J, Fleming C.A. and Cromberge G. The adsorption of gold cyanide onto activated carbon. 1. The kinetics of adsorption from pulps. JSAIMM, vol 84, No. 2, 1984).
95. Özer, A., Özer, D., Ibrahim Ekiz, H., 1999. Application of Freundlich and Langmuir models to multistage purification process to remove heavy metal ions by using Schizomeris leibleinii. Process Biochemistry 34, pp 919–927
96. Petersen, F.W. and Van Deventer, J.S.J., 1991. The influence of pH, dissolved oxygen and organics on the adsorption of metal cyanides on activated carbon, Chemical Engineering Science, Vol 46, No 12, pp 3053 – 3065.
97. Pleysier, R, Dai, X, Wingate, C.J, Jeffrey, M.I, Microtomography based identification of gold adsorption mechanisms, the measurement of activated carbon activity, and the effect of frothers on gold adsorption, Minerals Engineering 21 (2008) 453–462
98. Poinern, G.E.J., Senanayake, G, Shah, N, Thi-Le, X.N., Parkinson, G.M., Fawcett, D, 2011. Adsorption of the aurocyanide, $Au(CN)_2^-$ complex on granular activated carbons derived from macadamia nut shells – A preliminary study. Minerals Engineering 24 (2011) pp 1694 – 1702.
99. Puddephatt, R.J., 1978. The Chemistry of gold, Elsevier scientific publishing company. ISBN 0-444-41624-4 (vol 16)
100. Read, M.C., Glaser, J., Persson, I., Sandström, M., 1994, Rhodium(III) complexes with cyanide and Sulfur-donor ligands: Rhodium-103 nuclear magnetic resonance chemical shift correlations, Journal of the chemical society, Dalton transactions, paper 4/03327B, pp 3243 - 3248
101. Riley, R.P., 1991. Continuous Elution, Recent developments in In-Pulp technology, The South African Institute of Mining and Metallurgy, 7 – 8 October 1991
102. Roijals, O., Martl, V., Meinhardt, E., Cortina, J.L., Aguilar, M., Piccinini, N., Delorenzo (Eds.), R., 1996. Characterization of spent automotive catalyst residues for precious metal recycling using hydrometallurgical technologies. Chemical Industry and Environment Vol 2, Poloitecnico di Torino, pp 419 – 428.
103. Rose, M., 2006. Spacing measurements of lattice fringes in HRTEM images using digital darkfield decomposition. MSc thesis. The Graduate School at the University of Missouri.
104. Ruthven, D.M., 1984. Principles of adsorption and adsorption processes. John Wiley & Sons Inc.

105. Saari, P., Riekkola-Vanhanen, M., 2011. Talvivaara bioheap leaching process. The Southern African Institute of Mining and Metallurgy, Percolation Leaching: The status globally and in Southern Africa 2011. Misty Hills Conference Centre, Cradle of Humankind, Gauteng, 7 – 9 Nov.
106. Sceresini, B, Stephen, J, Base metal recovery by adsorption of cyano complexes on activated carbon, International Patent No WO 92/08812, 1992.
107. Schoeman, N., 1991. Carbon Management – some practical aspects, Recent developments in in-pulp technology, The South African Institute of Mining and Metallurgy, ISBN 1-874832-12-9, 7-8 Oct 1991
108. Schoeman, E. 2012. The recovery of platinum, palladium and gold from a cyanide heap solution, with use of ion exchange resins. MsC thesis, University of Stellenbosch, Dec 2012
109. Schoeman, E, Bradshaw, S.M., Akdogan, G, Eksteen, J.J., 2012. The recovery of platinum, palladium and gold from a cyanide heap solution, with use of ion exchange resins. The 5th international Platinum conference, the South African Institute of Mining and Metallurgy. 18 -20 September 2012. Sun City. Symposium series S72. Volume 2, pp 729 – 743.
110. Shams, K., Beiggy, M.R., and Gholamipour Shirazi,A. 2004. Platinum recovery from spent industrial dehydrogenation using cyanide leaching followed by ion exchange. *Applied Catalysis A: General*, vol. 258. pp. 227 – 234.
111. Shantz, R, Reich, J, 1978. A review of copper-cyanide metallurgy, Hydrometallurgy, 3, pp 99-109
112. Sharpe, A.G, 1976. The chemistry of cyano complexes of the transition metals, Academic press Inc. (London) ltd.
113. Shaw, D.A. and Hanratty, T.J. 1977. Influence of Schmidt Number on the Fluctuations of Turbulent Mass Transfer to a wall. AlChE Journal (Vol. 23, NO. 2), pp 160 – 169.
114. Shorrock, C.J., Jong, H, Batchelor, R.J., Leznoff, D.B., 2003. $Au(CN)_4^-$ as a Supramolecular building block for Heterobimetallic coordination polymers, Inorg. Chem. 2003, vol 42, pp 3917 – 3924.
115. Simanova, S.A, Shukarev, A.V, Lysenko, A.A., Grebennikov, S.F. & Astashkina, O.V., 2008. Adsorption of palladium, platinum and gold chloride complexes by carbon fibers with various structures. Fibre Chemistry, 40(4).
116. Song, H., Kim, F., Connor, S., Somorjai, G.A., Yang, P., 2005. Pt Nanocrystals: Shape Control and Langmuir-Blodgett Monolayer Formation. J. Phys. Chem. B, 109, pp 188-193.
117. Snyders, C.A, Mpinga, C.N, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2012. The adsorption and elution of platinum group metals (Pt, Pd and Au) from cyanide leach solutions using activated carbon, The South African Institute of Mining and Metallurgy, The fifth international Platinum Conference, 18 – 20 September.
118. Song, H., Kim, F., Connor, S., Somorjai, G.A., Yang, P., 2005. Pt Nanocrystals: Shape Control and Langmuir-Blodgett Monolayer Formation. J. Phys. Chem. B, 109, pp 188-193.
119. Souza, C., Majuste, D., Ciminelli, V.S.T., 2014. Effects of surface properties of activated carbon on the adsorption mechanism of copper cyanocomplexes. Hydrometallurgy, Vol. 142, pp 1 – 11.
120. Stange, W, The process design of gold leaching and carbon in pulp circuits, The Journal of The South African Institute of Mining and Metallurgy January/February 1999, pp 13 - 25
121. Staunton, W.P., 2005. Carbon-in-pulp. Chapter 23. Developments in mineral processing. Vol 15. Elsevier. pp 562 – 587
122. Steinfeld, J.I., Francisco, J.S., Hase W.L., 1998. Chemical Kinetics and Dynamics, second edition. Prentice Hall, Upper Saddle River, New Jersey 07458.
123. Tu, Z, Lu, S, Chang, X, Li, Z, Hu, Z, Zhang, L, Tian, H, Selective solid-phase extraction and separation of trace gold, palladium and platinum using activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate, Microchim Acta (2011) 173: 231 -329
124. Tsuchida, N, Muir, D.M., 1986. Studies on Role of Oxygen in the adsorption of $Au(CN)_2^-$ and $Ag(CN)_2^-$ onto activated carbon. Metallurgical Transactions B, Vol 17B, September 1986, pp 529 – 533.
125. Van der Merwe, P.F., 1991. Fundamentals of the elution of gold from activated carbon, PhD thesis, University of Stellenbosch, June.

126. Van der Merwe, P.F., Van Deventer, J.S.J., 1988. The influence of oxygen on the adsorption of metal cyanides on activated carbon, Chem. Eng. Comm. Vol 65, pp 121 - 138
127. Van Deventer, J.S.J, 1984. Kintetic model for the adsorption of metal cyanides onto activated charcoal, PhD dissertation.
128. Van Deventer, J.S.J., Liebenberg, S.P., 2003. The role of cyanide in the multi-component elution of cyanide complexes from activated carbon, The European Journal of Mineral processing and environmental protection, vol 3, nr 3, 1303 – 0868, 2003 pp 261 - 269
129. Van Deventer, J.S.J, Ross, V.E., 1991. The dynamic simulation of carbon-in-pulp systems: A review of recent developments, Minerals Engineering, Vol. 4, Nos 7-11, pp. 667-681, 1991
130. Van Deventer, J.S.J., Van der Merwe, P.F., 1993 (a). The Reversibility of adsorption of gold cyanide on activated carbon, Metallurgical transactions B, Volume 24B, June 1993, pp 433 – 440.
131. Van Deventer, J.S.J, Van der Merwe, P.F, 1993 (b). The effect of temperature on the desorption of gold cyanide from activated carbon, Thermochimica Acta, 221, 1993, 99 – 113
132. Van Deventer, J.S.J, Van der Merwe, P.F, 1994 (a). Factors affecting the elution of gold cyanide from activated carbon, Minerals Engineering, Vol. 7, No. I, pp. 71-86
133. Van Deventer, J.S.J, Van der Merwe, P.F, 1994 (b). The mechanism of elution of gold cyanide from activated carbon, Metallurgical and materials transactions B, Vol 25 B, December, pp 829 – 838.
134. Vegter, N.M, The distribution of gold in activated carbon during adsorption from cyanide solutions, Hydrometallurgy, 30 (1992) 229-242
135. Versiane, A., Ciminelli, V., 2000. Application of ion exchange resins in gold hydrometallurgy: a tool for cyanide recycling. Solvent Extraction and Ion Exchange, vol. 18, no. 3, pp. 567 -582.
136. Vorob'ev-Desyatovskii, N.V., Kubyshkin, S.A., Ibragimova, R.I., Kaichev, V.V., Dubrovskii, Ya. A., Babakov, V.N., Pichugina, D.A. 2012. Study of sorption of platinum and palladium cyanometallate complexes as the key to understanding the mechanism of binding the $[Au(CN)2]^-$ anion with carbon adsorbents. Russian Journal of General Chemistry, vol. 82, no. 3. pp. 384–397
137. Woollacot, L.C, Nino de Guzman, G, 1993. The combined influence of oxygen and cyanide on adsorption isotherms in carbon-based gold extraction systems, Minerals Engineering, Vol. 6, No. 3, pp. 251-265, 1993
138. Wulfsberg, G., 1991. Principles of descriptive inorganic chemistry. University Science books. ISBN 0-935702-66-0, pp 22
139. Yin, X., Opara, A., Du, H., Miller, J.D., 2011. Molecular dynamics simulations of metal–cyanide complexes: Fundamental considerations in gold hydrometallurgy. Hydrometallurgy, Vol. 106, pp 64 – 70.
140. Zhang, Y, Fang, Z, Muhammed, M, 1997. On the solution chemistry of cyanidation of gold and silver bearing sulphide ores. A critical evaluation of thermodynamic calculations. Hydrometallurgy 46, pp 251 – 269.

Appendix A

Additional graphs, tables and information

Additional graphs

Transmission Electron Miscroscopy (TEM)

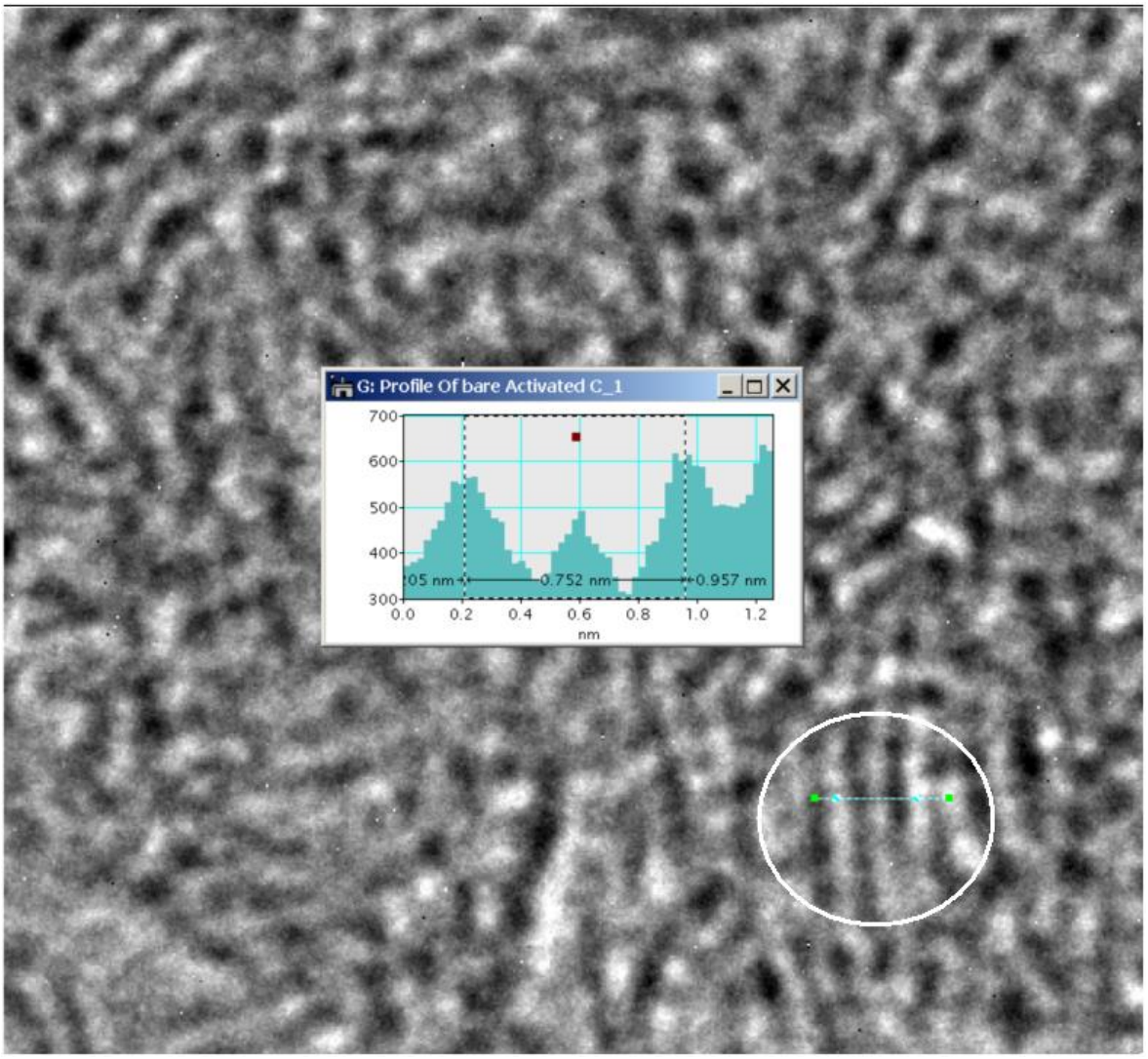


Figure A.104: TEM image of unloaded activated carbon with a interlayer spacing between lattice fringes of 2.5 Å in the area indicated by the white circle.

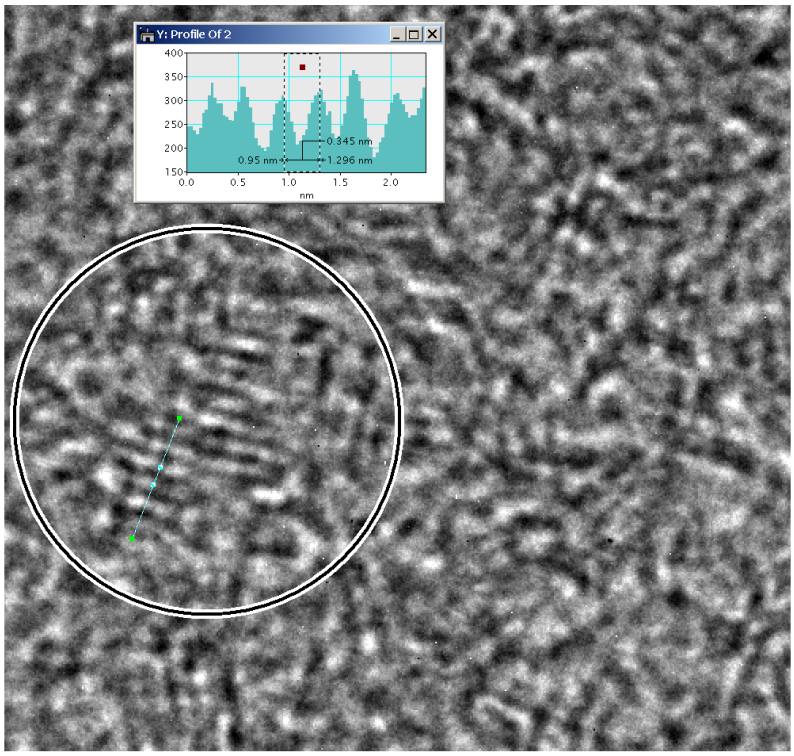


Figure A.105: TEM image of activated carbon loaded with aurocyanide revealing a structure with a interlayer spacing between lattice fringes of 3.45 Å in the area indicated by the circle.

```
Au-L        74.418      40.028
Au-M        18.790      42.684

Input FWHM = 134 eV @ 5.9 keV
Measured FWHM = 134.000 eV @ 5.9 keV
Calibration: 5.02273 eV/ch, 19.6194 eV at channel 0
Accelerating voltage: 200 kV
Alpha tilt: 15 degrees


***Quantification Results***

Correction method: None
```

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor
C(K)	92.61	96.65	0.81	0.26	3.940
O(K)	2.94	2.30	0.09	0.49	1.974
Cl(K)	0.47	0.16	0.02	0.95	1.063
Ca(K)	2.41	0.75	0.06	0.98	1.083
Pd(L)	0.26	0.03	0.02	0.95	2.627
Pt(L)	0.62	0.03	0.07	0.75	5.547
Au(L)	0.66	0.04	0.07	0.75	5.653

Figure A. 106: TEM-EDX analysis for the entire image as shown in Figure 4.29

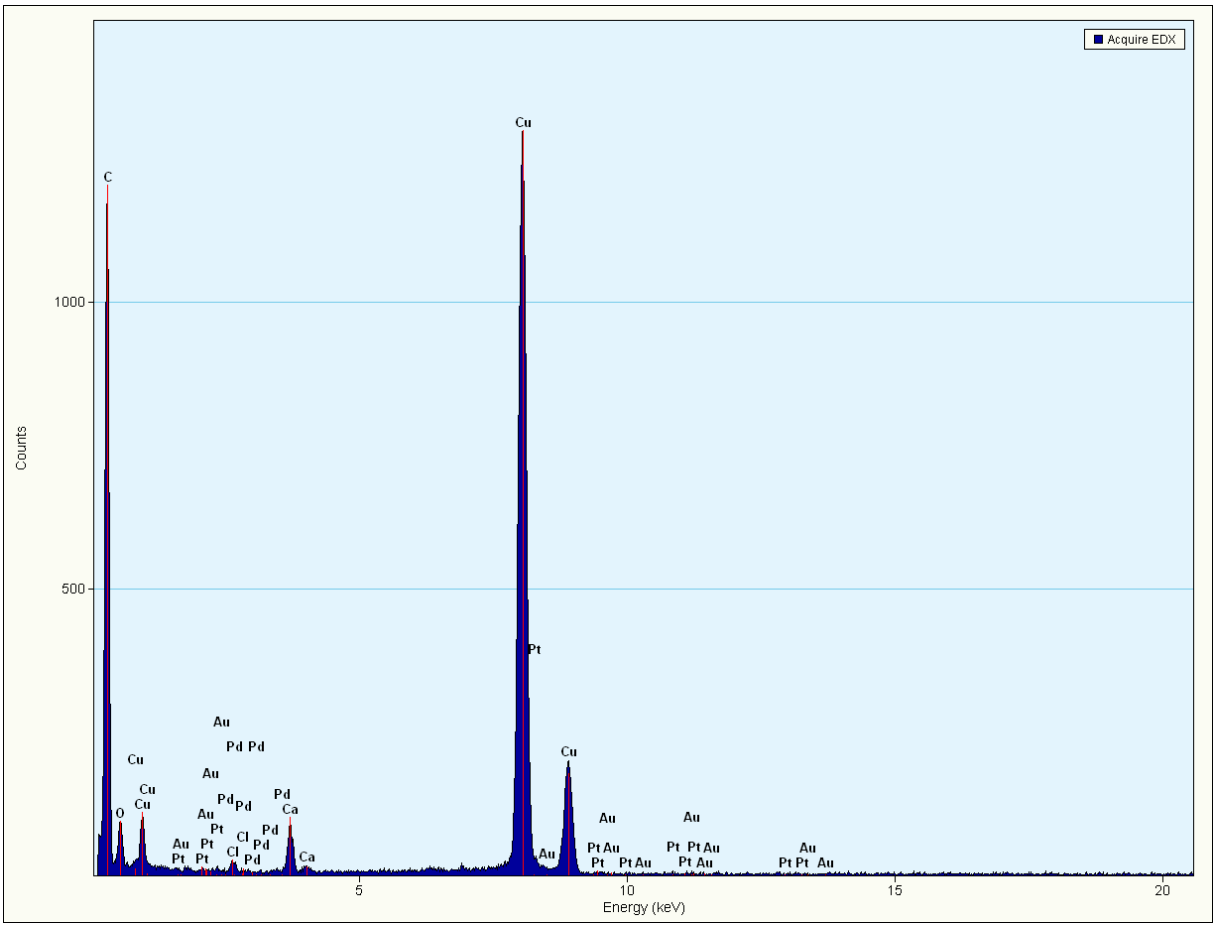


Figure A.107: TEM-EDX analysis for the entire image shown in Figure 4.29

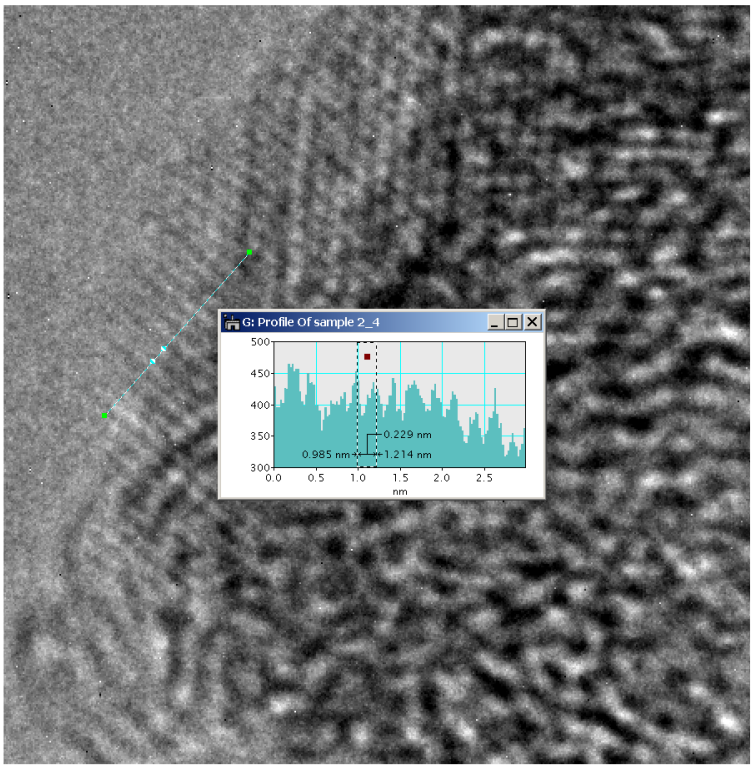


Figure A.108: TEM image of activated carbon loaded with platinum cyanide revealing a structure with a interlayer spacing between lattice fringes of 2.22 Å. (9 peaks between 1 and 3 nm resulting in an average of 2.22 Å)

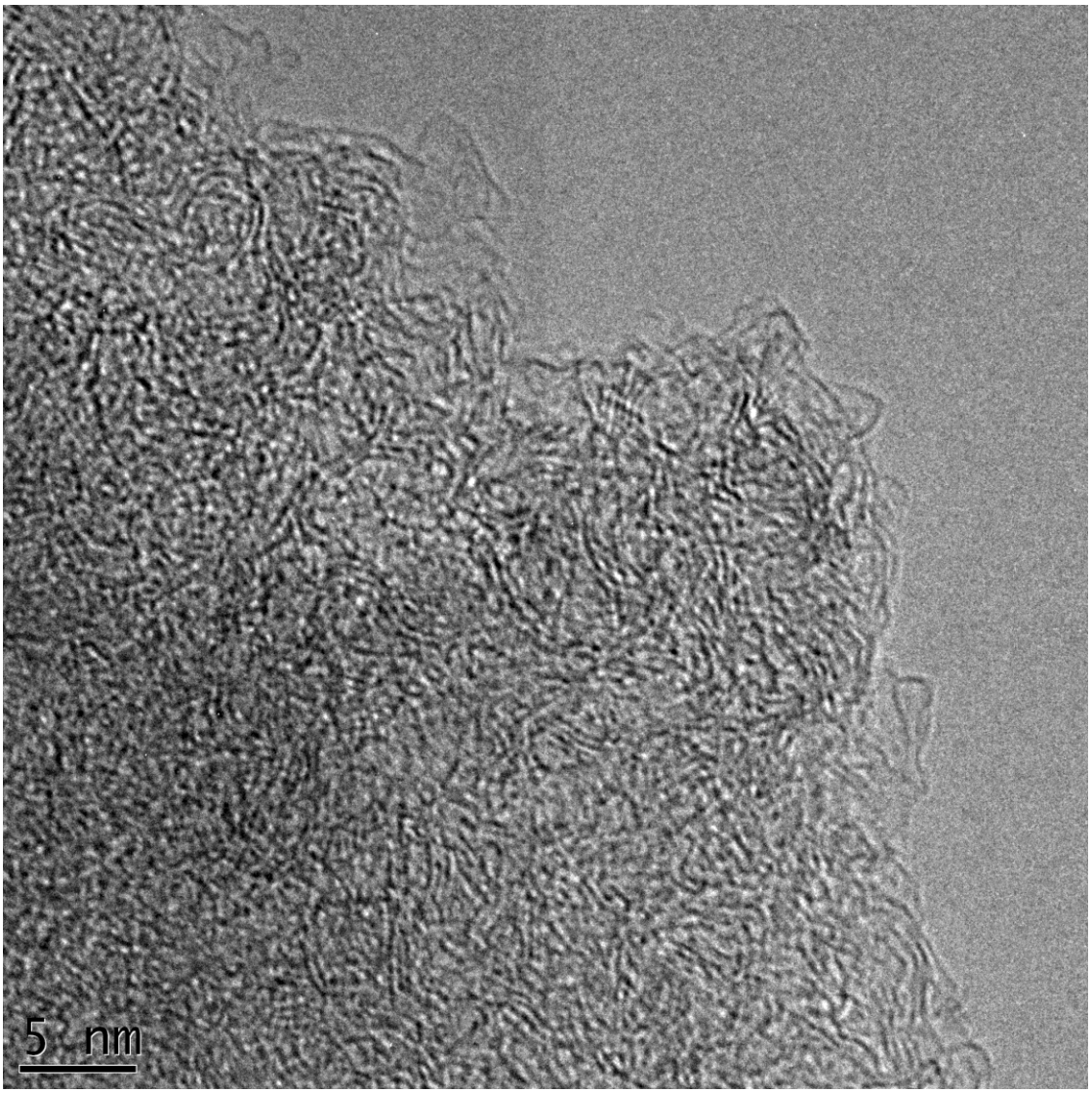


Figure A.109: TEM image of activated carbon loaded with palladium cyanide. No specific structure other than that of activated carbon could be identified.

Accelerating voltage: 200 kV
Alpha tilt: 15 degrees

Quantification Results

Correction method: None

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor
C(K)	96.03	97.73	0.69	0.26	3.940
O(K)	2.39	1.82	0.07	0.49	1.974
Cl(K)	0.68	0.23	0.02	0.95	1.063
Ca(K)	0.52	0.15	0.02	0.98	1.083
Pd(L)	0.35	0.04	0.02	0.95	2.627
Pt(L)	0.00	0.00	100.00	0.75	5.547
Au(L)	0.00	0.00	100.00	0.75	5.653

Figure A.110: TEM-EDX analysis for the entire image shown in Figure A.109

Adsorption to equilibrium

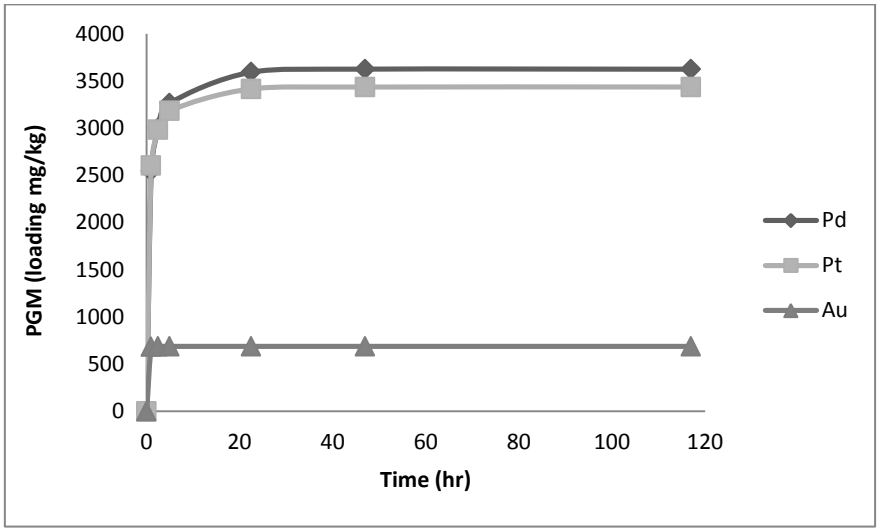


Figure A.111: Activated carbon loading from a high concentration PGM (30.8 mg/L Pd, 28.7 mg/L Pt, 5.5 mg/L Au) solution. (CN = 0, pH = 9.5, Temperature = 25°C)

Adsorption at temperature

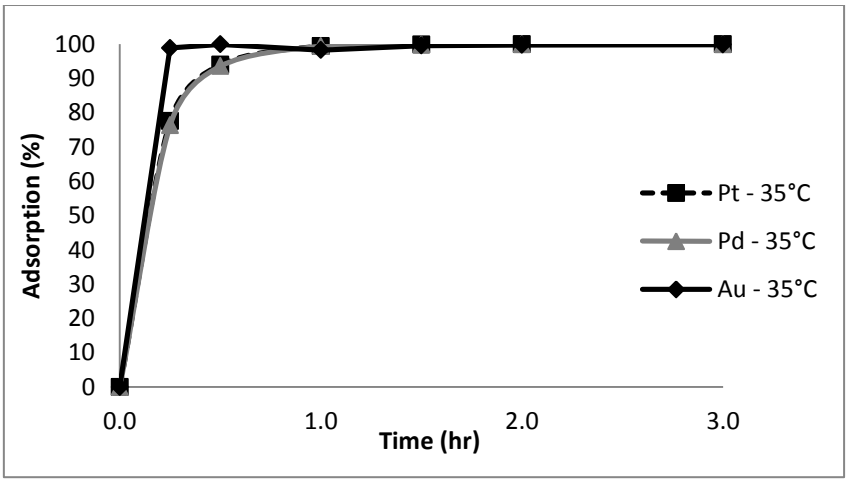


Figure A.112: Adsorption of Pt, Pd and Au at 35°C in a stirred vessel.

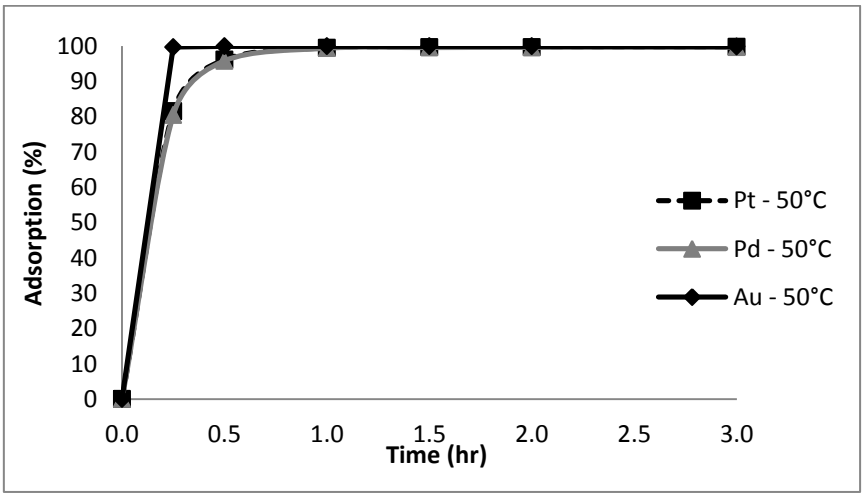


Figure A.113: Adsorption of Pt, Pd and Au at 50°C in a stirred vessel.

Base Metal adsorption

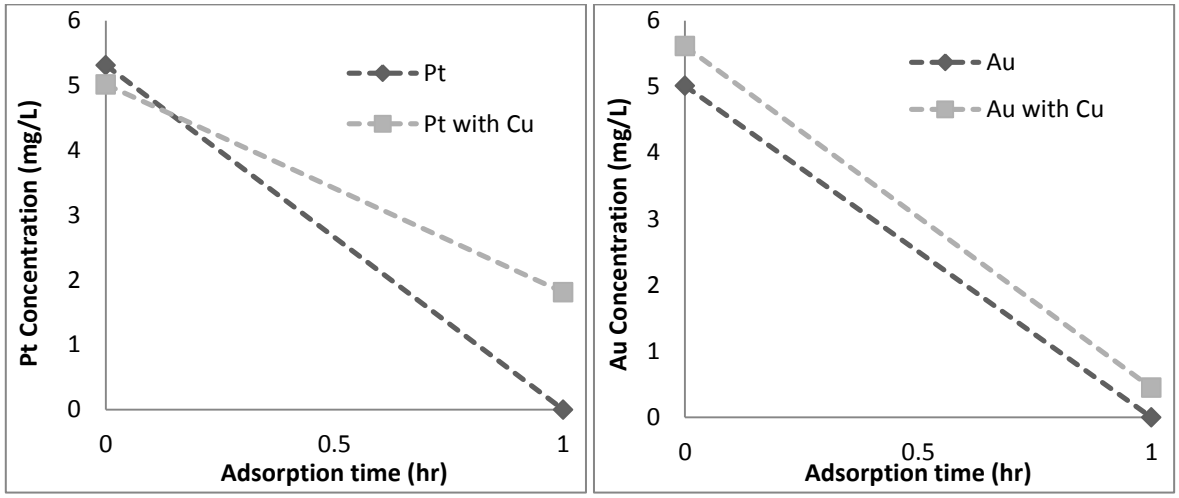


Figure A.114: Pt and Au adsorption with and without copper addition (pH = 9.5, [NaCN] =50, Pt = 5 mg/L, Pd = 5mg/L, Au 5mg/L)

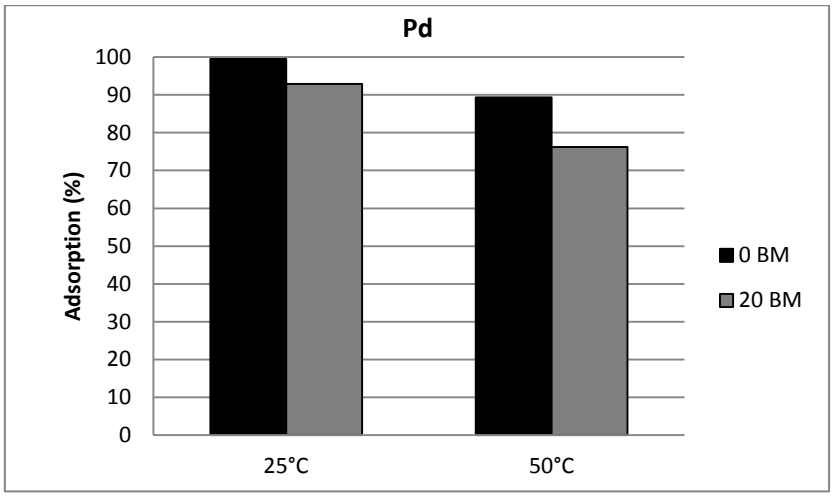


Figure A.115: The effect of temperature and base metals on the total adsorption of palladium after 4 consecutive loadings from a pregnant PGM leach solution. (pH = 9.5, [CN] = 0mg/L, Pt = 1 mg/L, Pd = 0.15, Au = 0.22mg/L)

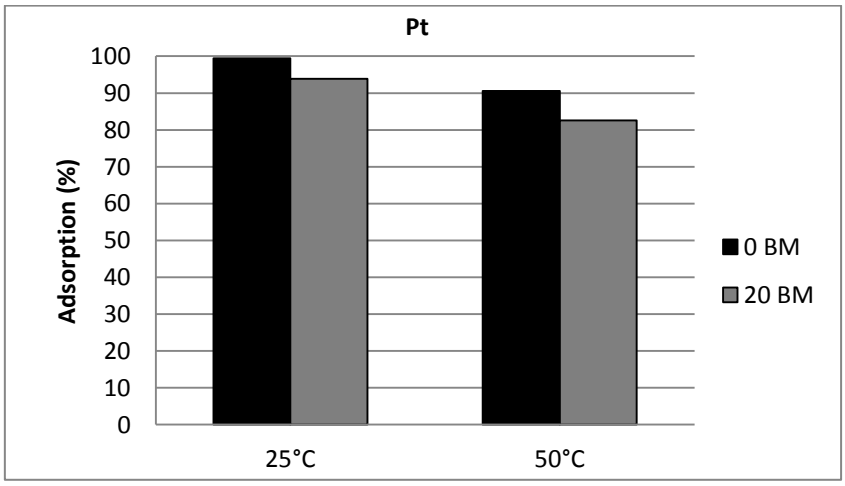


Figure A.116: The effect of temperature and base metals on the total adsorption of platinum after 4 consecutive loadings from a pregnant PGM leach solution. (pH = 9.5, [CN] = 0mg/L, Pt = 1 mg/L, Pd = 0.15, Au = 0.22mg/L)

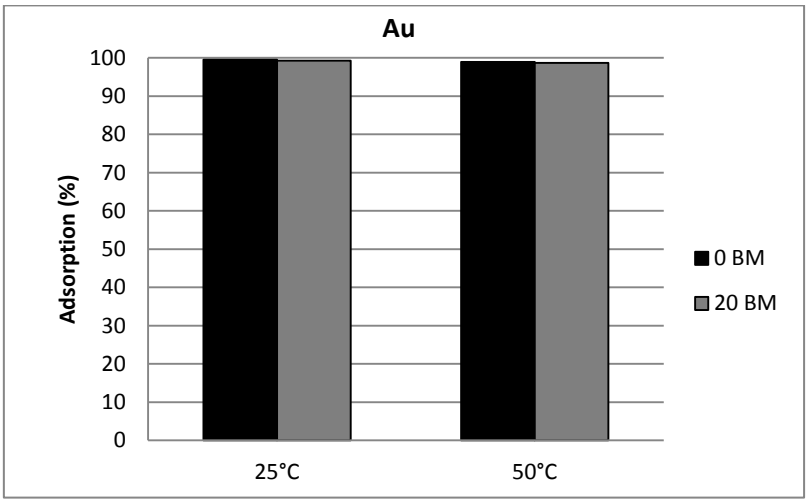


Figure A.117: The effect of temperature and base metals on the total adsorption of gold after 4 consecutive loadings from a pregnant PGM leach solution. (pH = 9.5, [CN] = 0mg/L, Pt = 1 mg/L, Pd = 0.15, Au = 0.22mg/L)

Elution

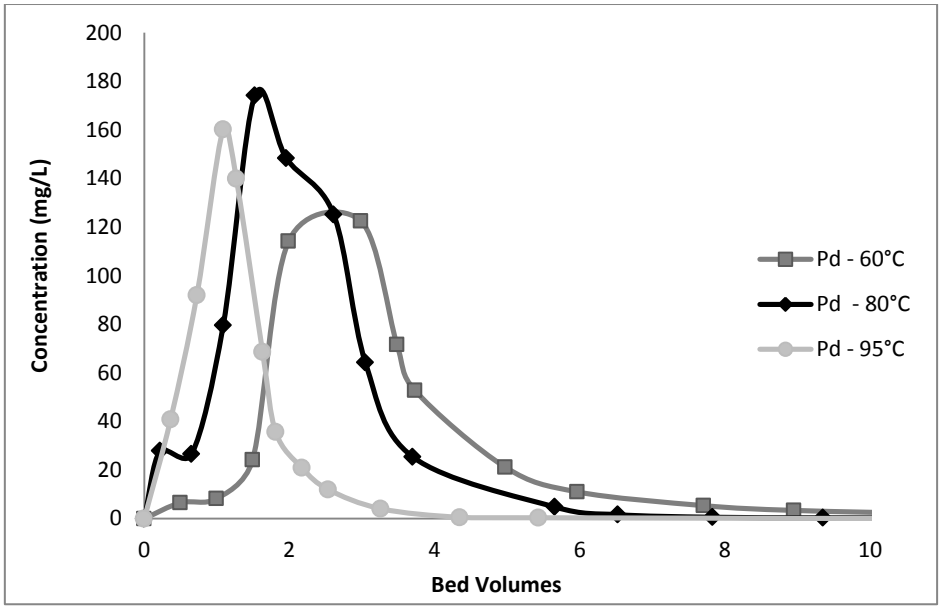


Figure A.118: Elution profile for Pd at varying temperatures at 2% NaCN and 0.6% NaOH pre-treatment. The carbon loading for the elution at 95°C were lower at 276 mg/kg compared to ≈ 650 mg/kg for the elutions performed at 60 and 80°C.

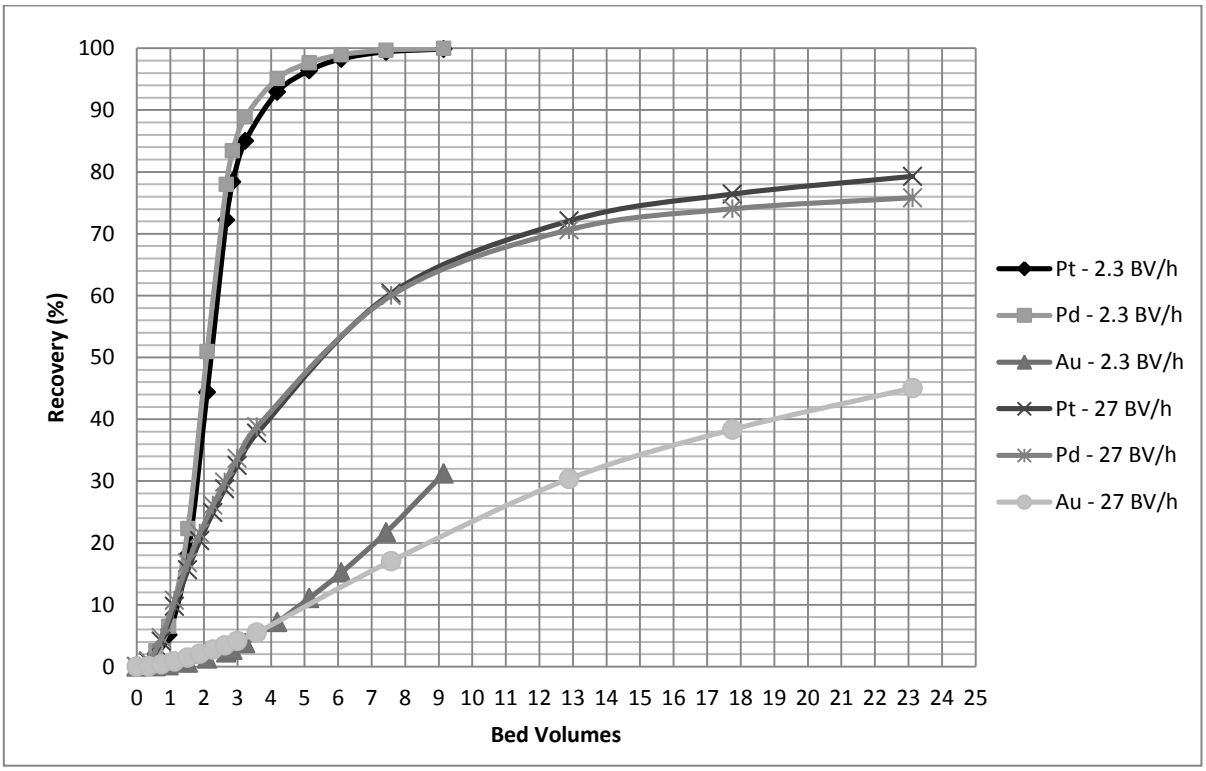


Figure A.119: Elution recoveries of Pt, Pd and Au at low (2.3BV/h) and high (27 BV/h) elution flow rates in a glass column at 80°C and atmospheric pressure.

Elution in the presence of Copper

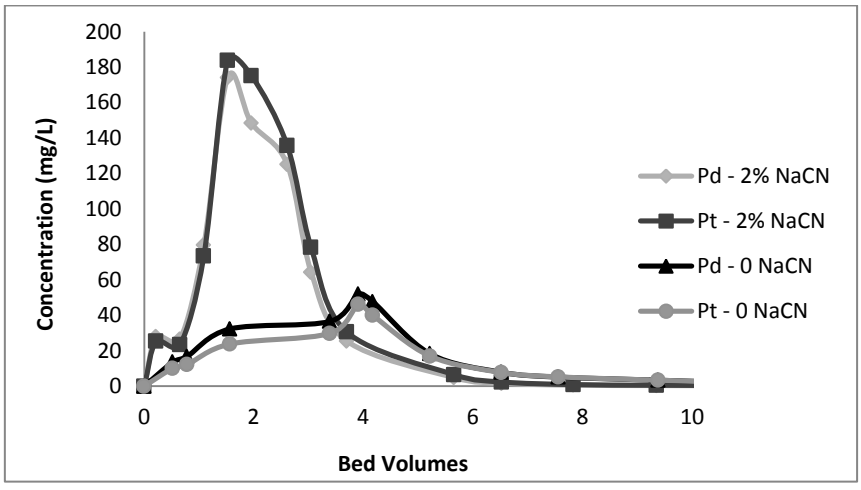


Figure A.120: Comparison of Pt and Pd elution with and without cyanide pre-treatment in the presence of copper cyanide.

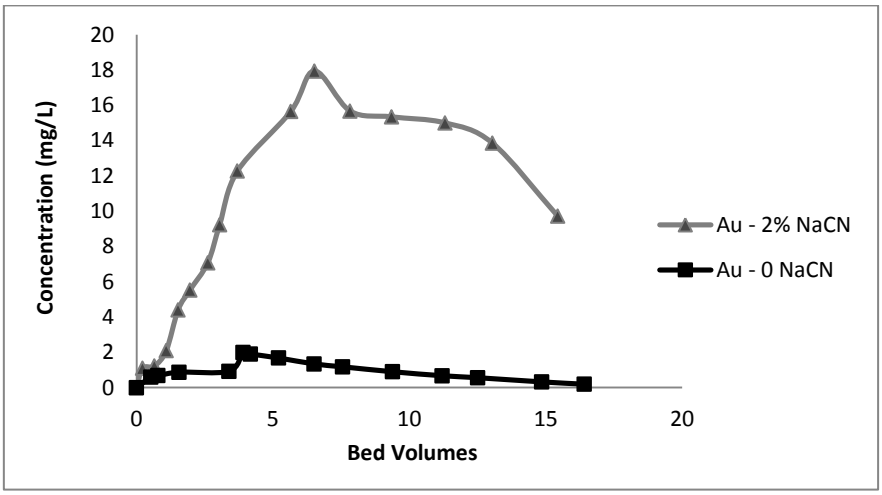


Figure A.121: Comparison of a) Au and b) Cu elution with and without cyanide pre-treatment

Elution in the presence of thiocyanide (KSCN)

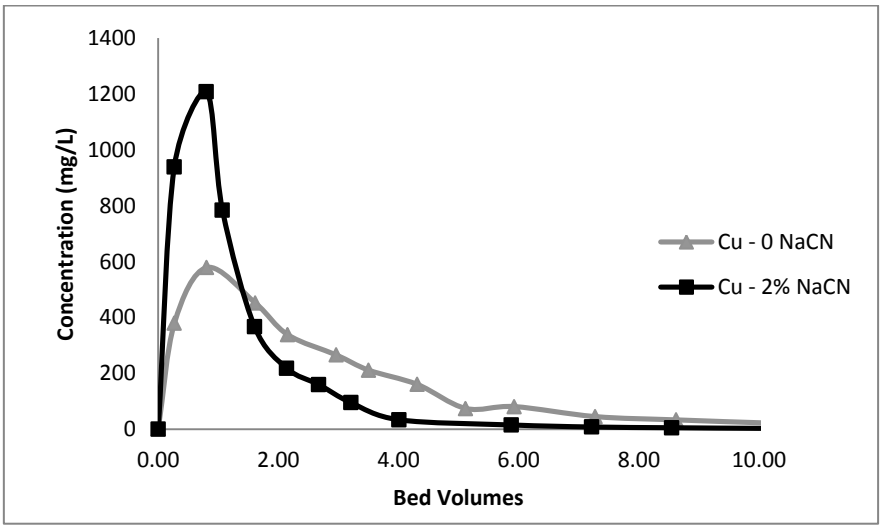


Figure A.122: Comparison of Cu elution with and without cyanide pre-treatment in the presence of KSCN

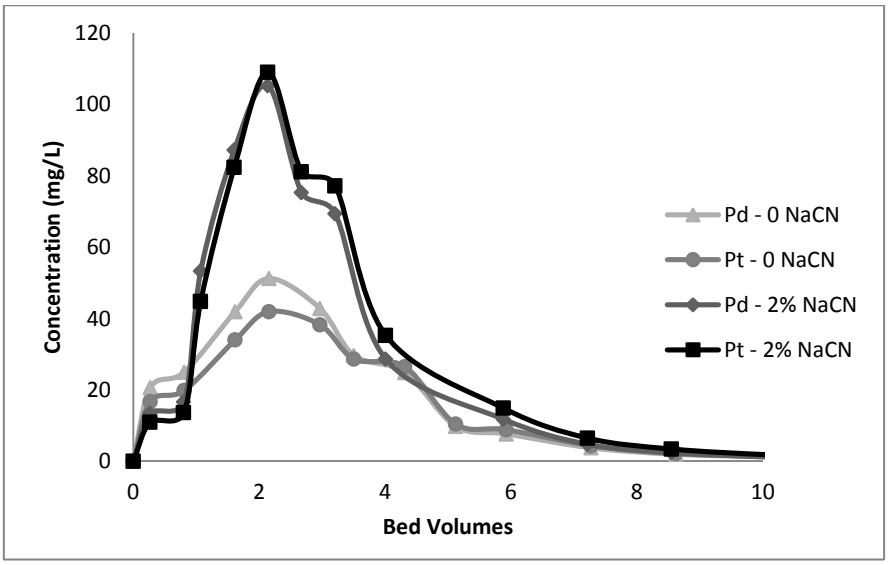


Figure A.123: Comparison of Pt and Pd elution with and without cyanide pre-treatment in the presence of copper cyanide and KSCN.

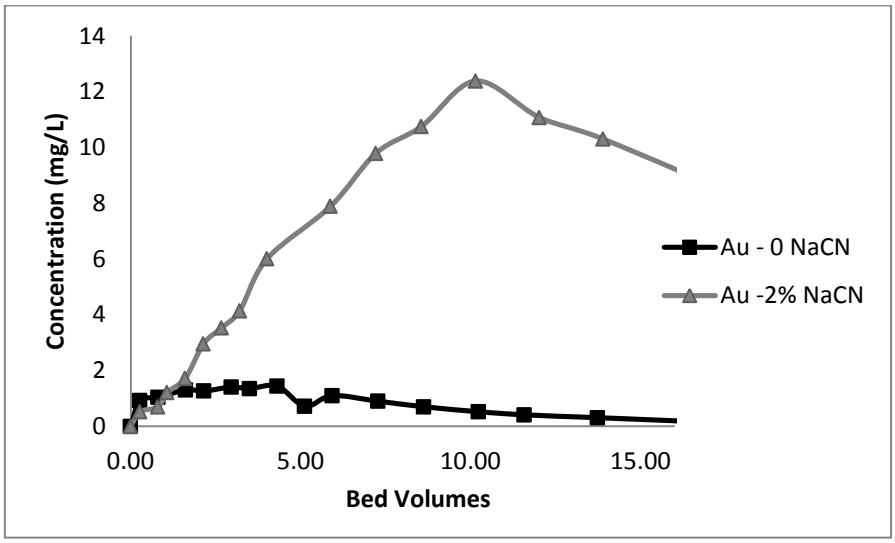


Figure A.124: Comparison of Au elution with and without cyanide pre-treatment in the presence of copper cyanide and KSCN.

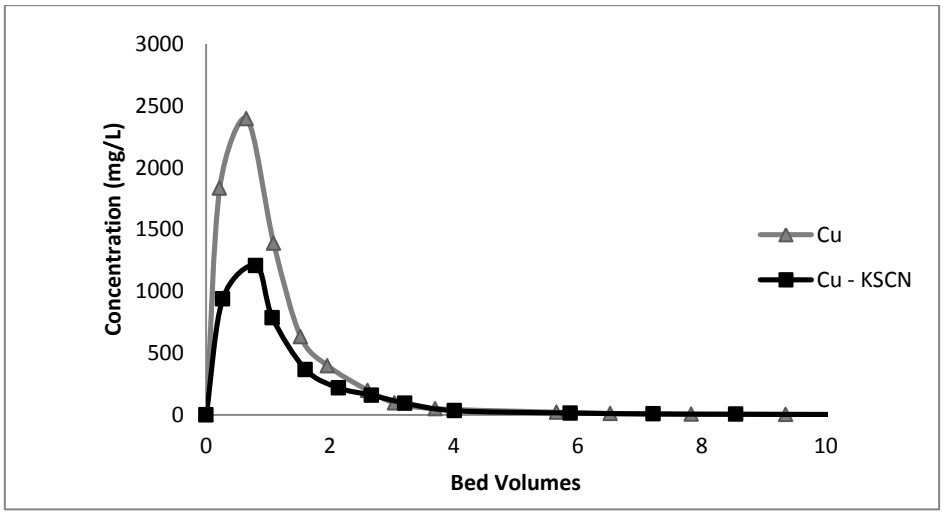


Figure A.125: The elution recovery of Cu in the presence of KSCN salt (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH and elution at 80°C.)

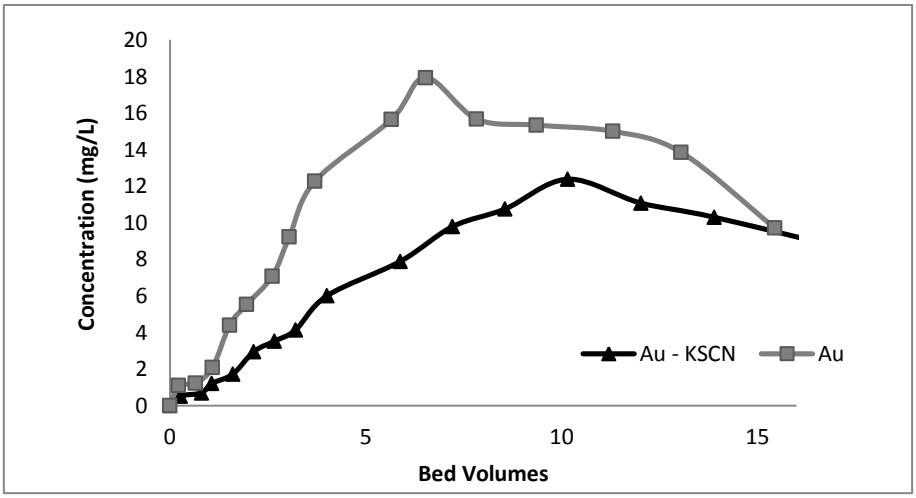


Figure A.126: The elution recovery of Au in the presence of KSCN salt (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH and elution at 80°C.

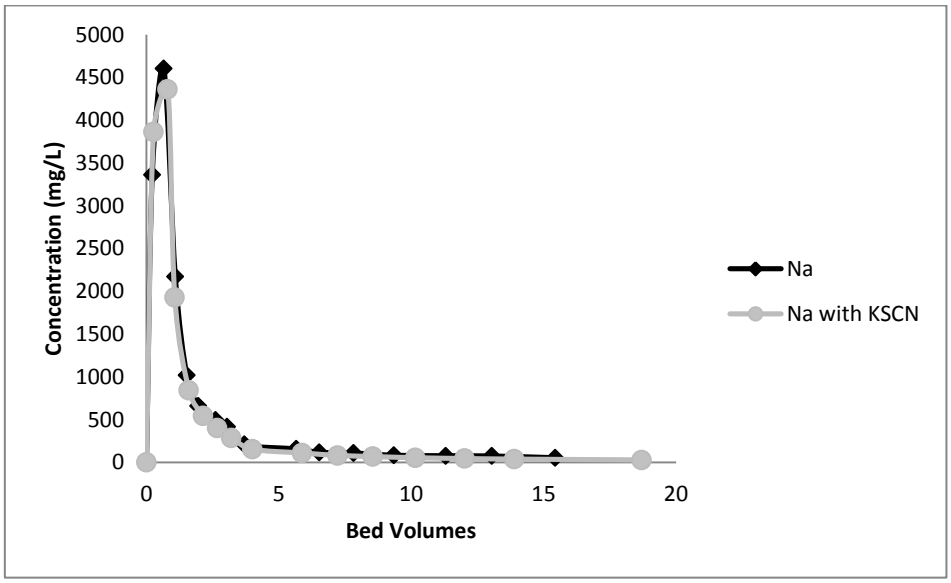


Figure A.127: Comparison of Na elution profiles for the experiments with and without KSCN added.

PGMs in the pre-treatment step

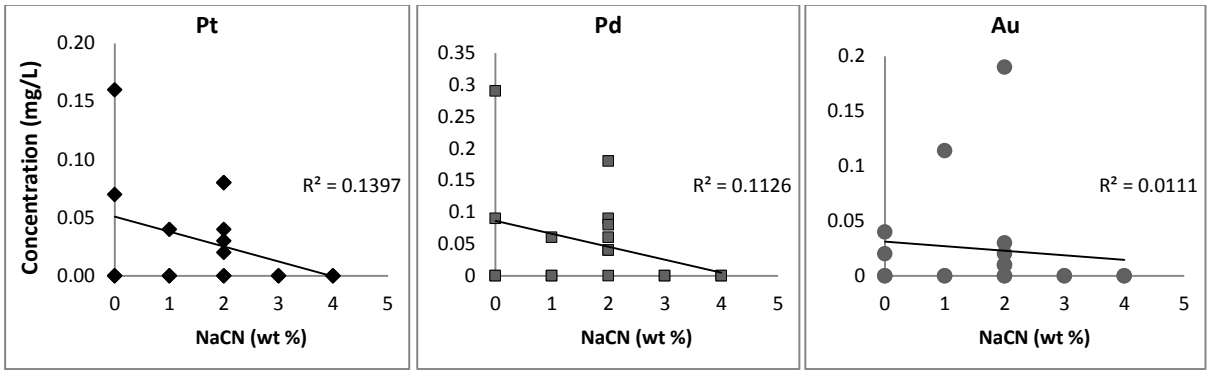


Figure A.128: Pt, Pd and Au concentration vs the cyanide concentration in the pre-treatment solution at 0.55% NaOH

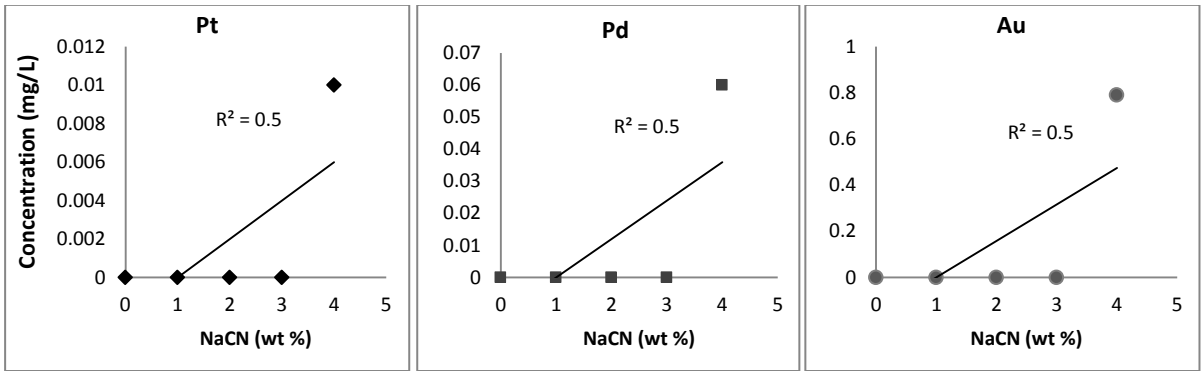


Figure A.129: Pt, Pd and Au concentration vs the cyanide concentration in the pre-treatment solution at 1.1% NaOH

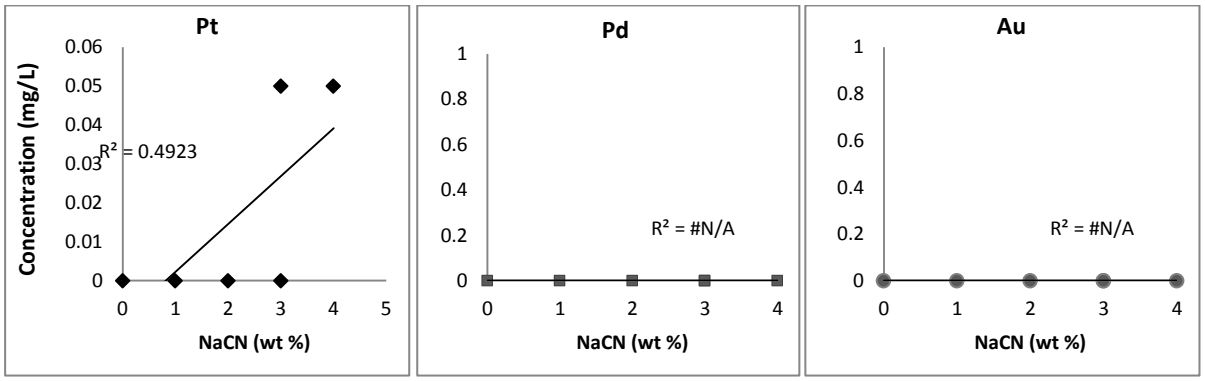


Figure A.130: Pt, Pd and Au concentration vs the cyanide concentration in the pre-treatment solution at 1.65% NaOH

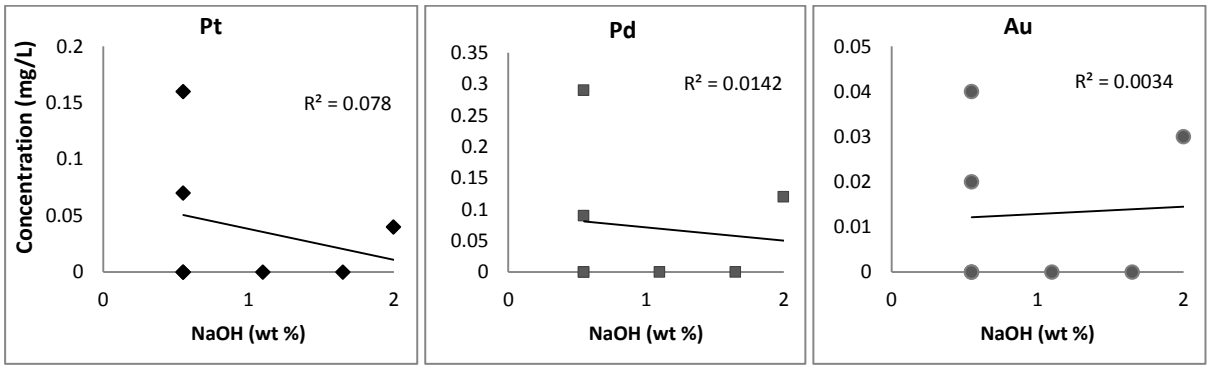


Figure A.131: Pt, Pd and Au concentration vs the NaOH concentration in the pre-treatment solution at 0% NaCN

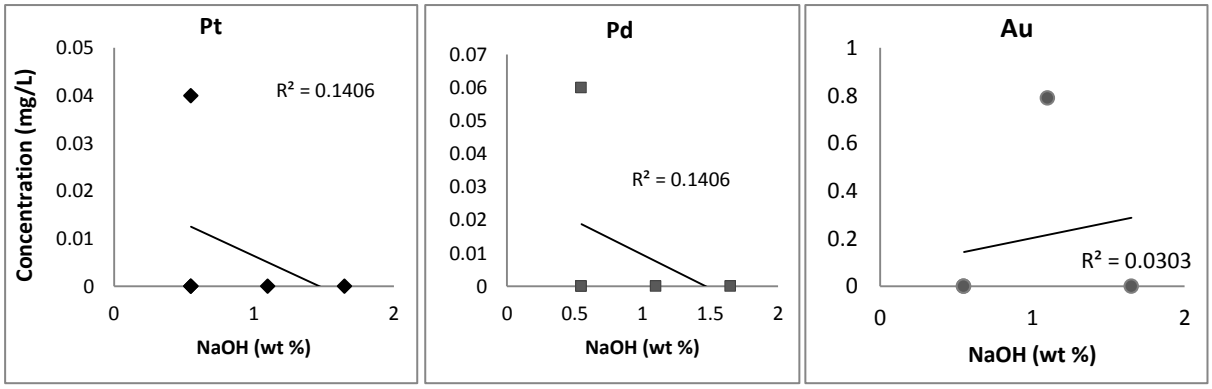


Figure A.132: Pt, Pd and Au concentration vs the NaOH concentration in the pre-treatment solution at 1% NaCN

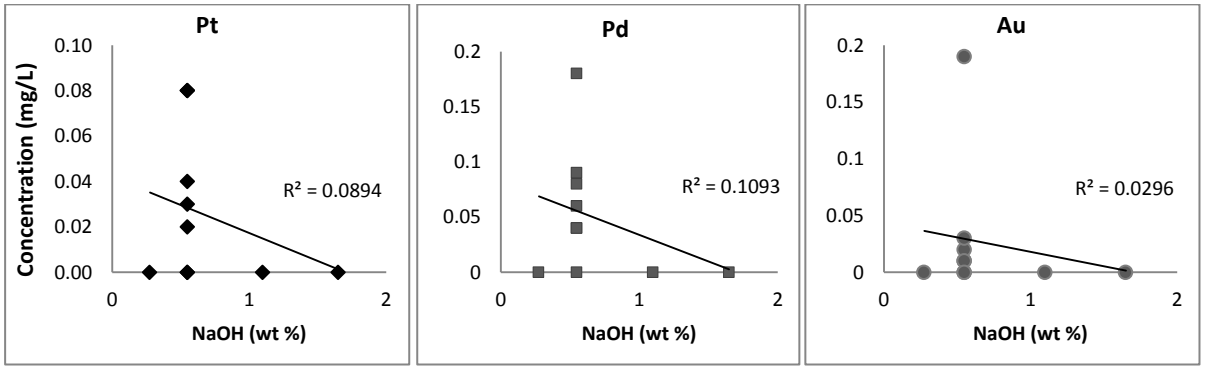


Figure A.133: Pt, Pd and Au concentration vs the NaOH concentration in the pre-treatment solution at 2% NaCN

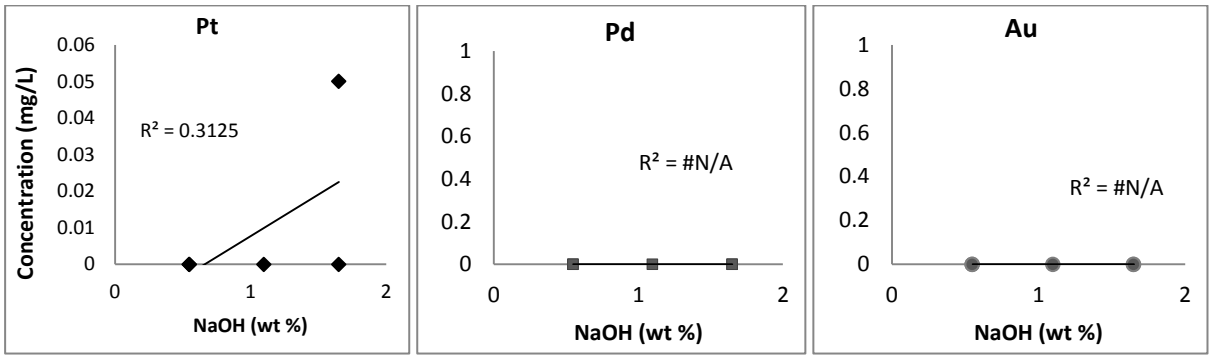


Figure A.134: Pt, Pd and Au concentration vs the NaOH concentration in the pre-treatment solution at 3% NaCN

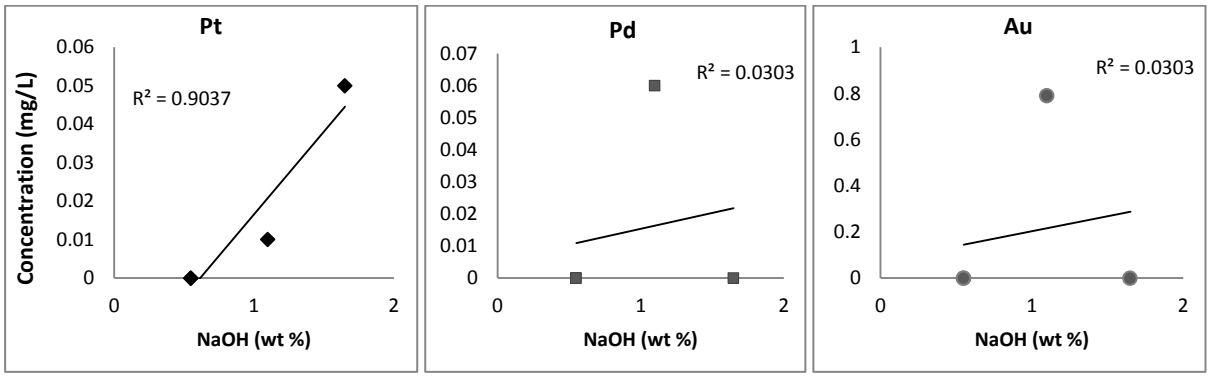


Figure A.135: Pt, Pd and Au concentration vs the NaOH concentration in the pre-treatment solution at 4% NaCN

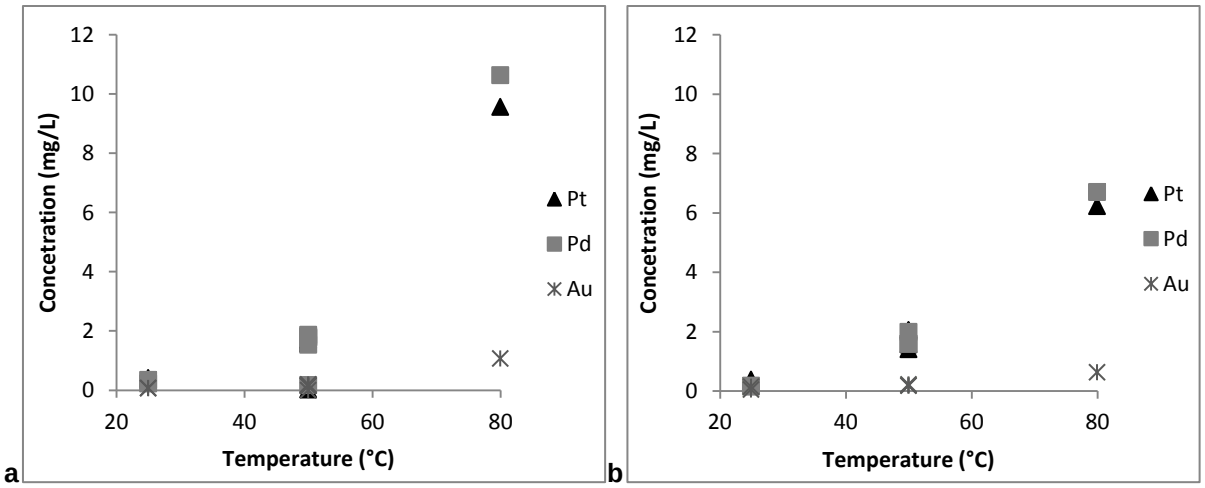


Figure A.136: PGMs reporting to the pre-treatment solution with rising temperatures at a stirring rate of a) 200rpm and b) no stirring. (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH)

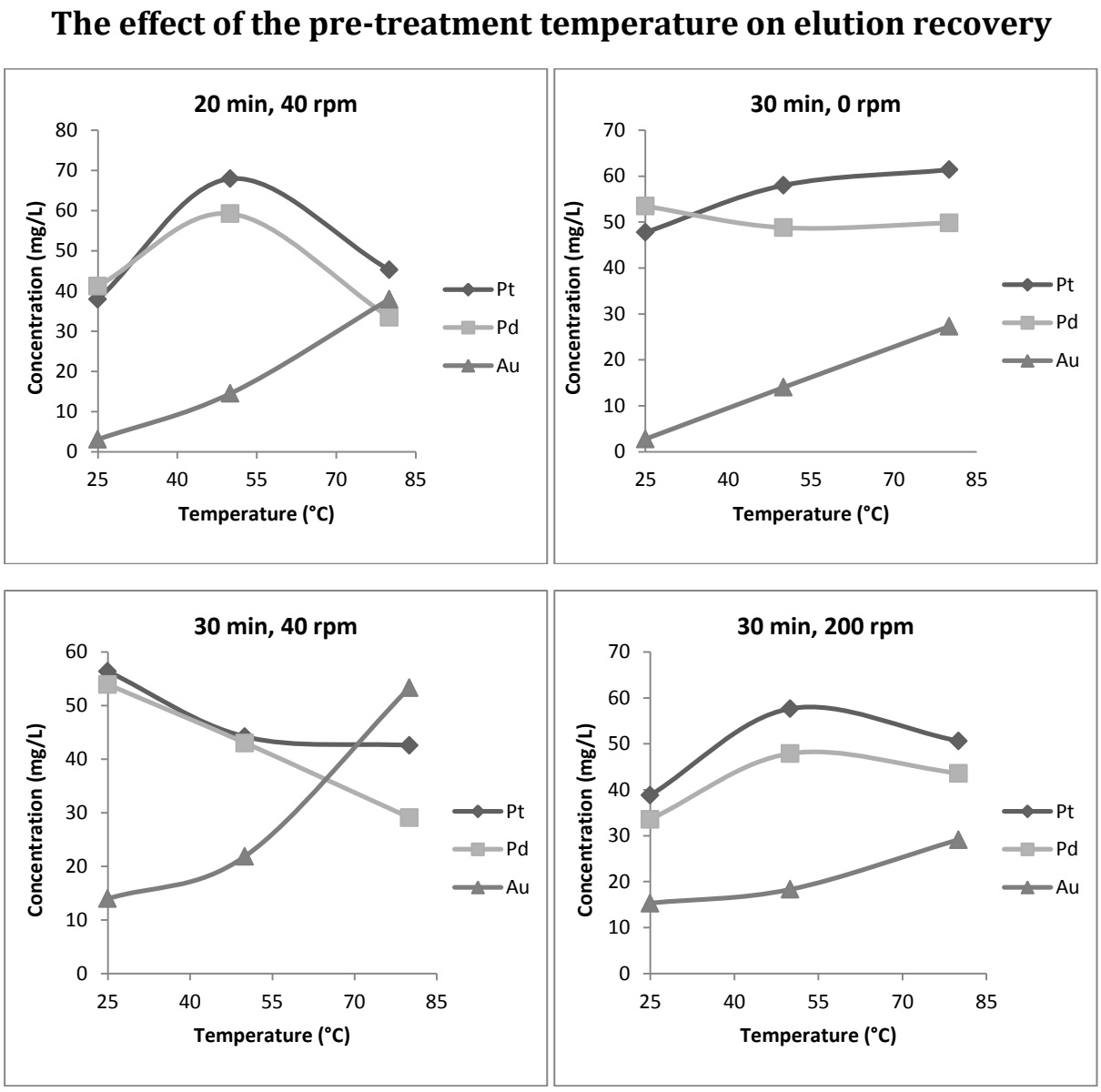


Figure A.137: The effect of the pre-treatment temperature on the elution recovery of Pt, Pd and Au at various pre-treatment times and stirring rates.

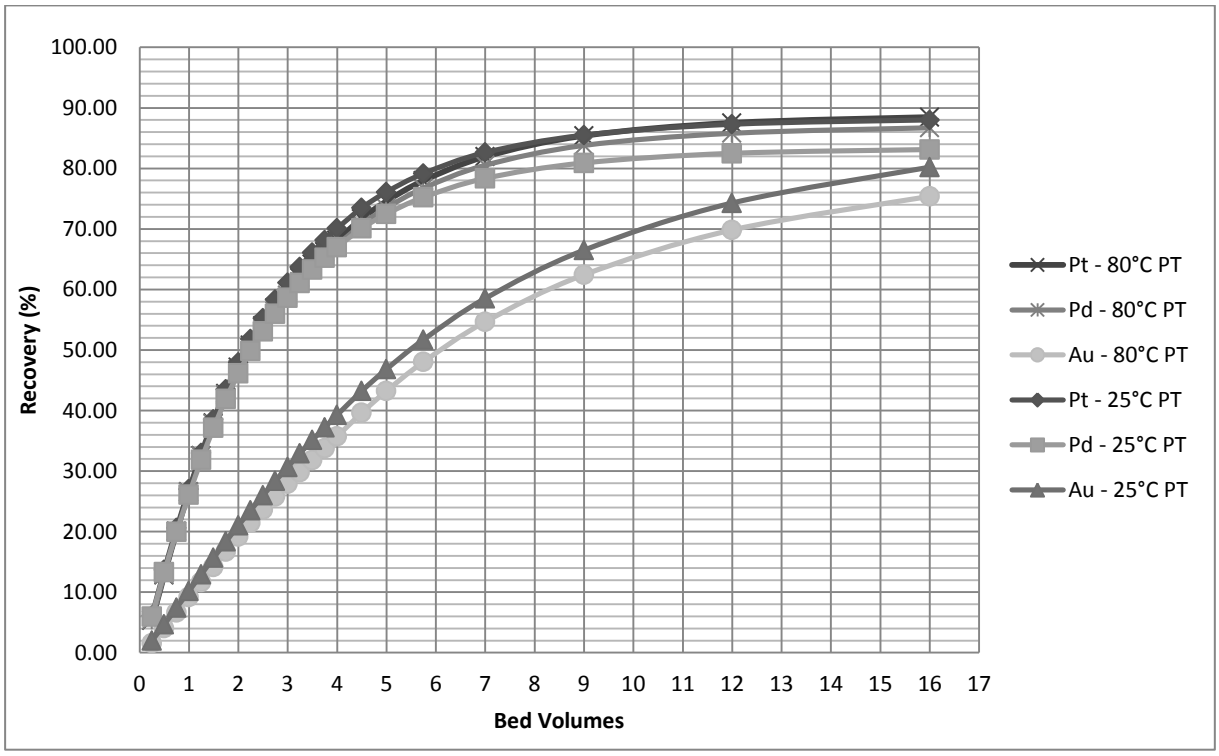


Figure A.138: Recovery profiles for the elution at 130°C but with pre-treatments (PT) at 25°C and 80°C. (230g/t Pd, 300mg/kg Pt, 500mg/kg Au loadings after pre-treatment with 2% NaCN and 0.55% NaOH)

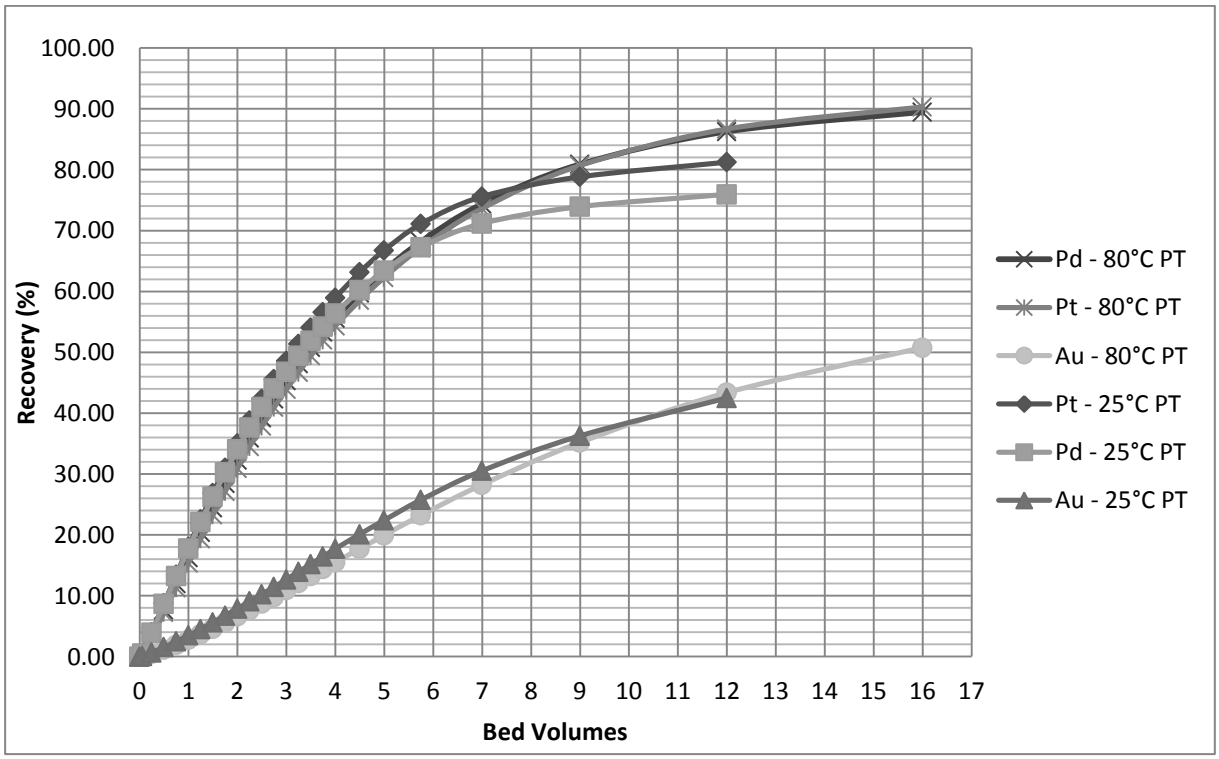


Figure A.139: Recovery profiles for the elution at 100°C but with pre-treatments (PT) at 25°C and 80°C. (230g/t Pd, 300mg/kg Pt, 500mg/kg Au loadings after pre-treatment with 2% NaCN and 0.55% NaOH)

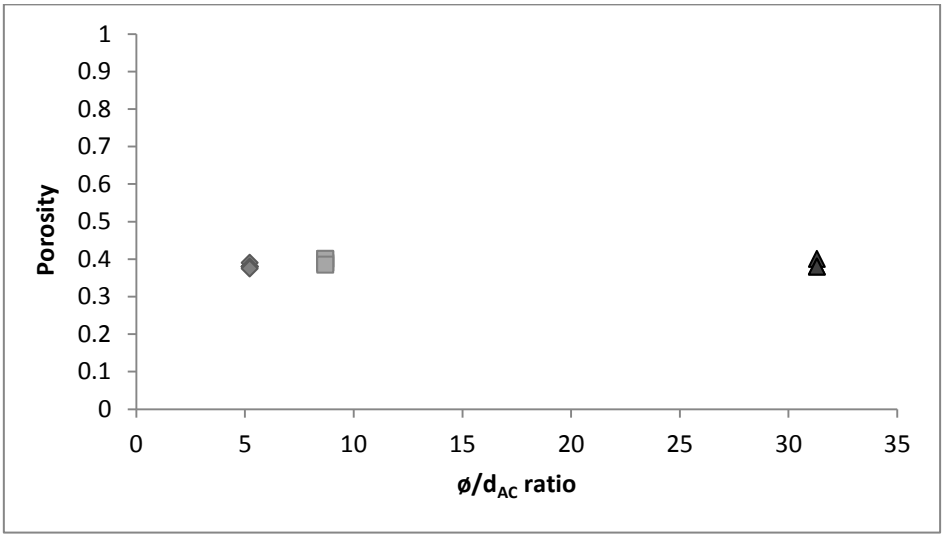


Figure A.140: Column porosity at various ø/d_{AC} ratios

Table A.34: XRF analysis of activated carbon acid attrition

Component	Activated carbon content	
	Virgin	Acid washed
Pt	*	*
Pd	*	*
Rh	*	*
Au	*	*
Ni	90 ppm	80 ppm
Cu	**	**
K	8.20%	5.64%
Na	0.13%	0.07%
Cl	182 ppm	3879 ppm

Table A.35: Composition of pregnant leach solution from column test

Constituent	Concentration (mg/L)	Constituent	Concentration (mg/L)
Pt	0.150	Pb	0.01
Pd	0.380	Ca	18.500
Rh	0.010	Li	0.007
Ru	0.010	Na	6137
Ir	0.001	K	23.15
Au	0.100	Mg	1.67
Ag	0.040	NO_3^-	0.000
Cu	18.840	Cl^-	12.600
Co	< 1	CN^-	12.5
Ni	18.300	SCN^-	3670
Fe	47.300	S^{2-}	2.600
Zn	0.060	SO_4^{2-}	11230

Table A.36: PGMs reporting to the pre-treatment solution with at different pre-treatment times, stirring rates and temperatures. (650g/t of Pt, Pd and Au each, after pre-treatment with 2% NaCN and 0.55% NaOH)

Temp (°C)	Time (min)	Stirring (rpm)	Au	Pd	Pt
25	20	0	0.14	0.15	0.39
25	30	0	0.05	0.18	0.35
50	20	0	0.22	1.99	2.06
50	20	0	0.19	1.59	1.57
50	20	0	0.18	1.59	1.41
80	10	0	0.63	6.71	6.23
25	20	40	0.07	0.19	0.48
25	30	40	0.10	0.22	0.52
50	10	40	0.13	1.42	1.31
50	20	40	0.20	2.06	1.79
50	20	40	0.14	2.18	1.88
80	10	40	0.66	10.38	9.21
25	20	200	0.08	0.23	0.38
25	30	200	0.06	0.35	0.41
50	10	200	0.17	1.54	1.58
50	10	200	0.00	0.17	0.02
50	20	200	0.16	1.79	1.71
50	20	200	0.16	1.82	1.65
50	20	200	0.14	1.77	1.59
50	20	200	0.19	1.87	1.70
80	10	200	1.08	10.63	9.57

Table A.37: PGMs reporting to the pre-treatment solution at 80°C for 56g activated carbon in a 210mL pre-treatment solution (300 mg/kg of Pt, 230 mg/kg Pd and 500 mg/kg Au, after pre-treatment with 2% NaCN and 0.55% NaOH)

	Au	Pd	Pt
PT 120 H	0.15	2.13	1.36
PT 130 H	0.27	3.30	1.82
PT 100 H	0.19	2.73	1.45
PT 110 H	0.26	3.00	1.38
PT 120 HR	0.46	3.51	2.00

Water analysis

Table A.38: Detailed water analysis

	Quality Control			
	Cert Std value	Analysed	% Error	Water
Al	0.97	1	3.09	0.02
Ca	9.6	10.12	5.42	6.51
Fe	0.97	1.01	4.12	0.03
K	9.6	10.25	6.77	0.62
Mg	9.6	10.53	9.69	0.88
Na	9.6	10.3	7.29	7.56
Si	0.97	0.9	7.22	2.14
Mn	0.01	0.01	0.83	0.00
Co	0.01	0.01	16.76	nd
Ni	0.01	0.01	4.20	nd
Cu	0.01	0.01	18.39	0.03
Zn	0.09	0.10	2.77	0.14
Au	0.99	1.08	9.39	0.08
Pd				nd
Pt				nd

Table A.39: Water analysis for each elution experiment

Nr	Exp	Au	Cu	Na	Pd	Pt
1	NB2	< 0.001	0.05	0.6	0.01	< 0.001
2	NC2	0.00	0.07	0.7	< 0.001	< 0.001
3	ND2	< 0.001	0.03	0.6	< 0.001	< 0.001
4	NE2	< 0.001	0.04	0.6	< 0.001	< 0.001
5	NF2	0.00	4.89	4.34	< 0.001	< 0.001
6	NG2	< 0.001	3.20	6.1	< 0.001	< 0.001
7	NH2	< 0.001	0.04	1.2	< 0.001	< 0.001
8	NI2	0.0253	5.144	10.34	0.0373	0.1181
9	NJ2	0.03	1.17	3.27	nd	nd
10	NK2	nd	0.08	0.66	nd	nd
11	NL2	nd	0.06	0.53	nd	nd
12	NM2	nd	0.04	0.42	nd	nd
13	NN2	nd	0.06	0.51	nd	0.01
14	AK2	nd		3.39	0.01	0.02
15	O2	nd	0.01	0.43	nd	nd
16	P2	nd	0.01	0.54	nd	nd
17	Q2	nd	0.01	0.58	nd	nd
18	R:2	nd	0.02	0.68	nd	nd
19	S2	0.02	0.01	0.66	nd	nd
20	T2	0.00	0.02	0.79	nd	nd
21	U2	nd	0.02	0.65	nd	nd
22	V2	0.02	0.03	0.66	nd	nd
23	W2	nd	0.01	0.60	nd	nd
24	X2	0.02	0.02	0.71	nd	nd
25	Y2	0.02	0.01	1.34	nd	nd
26	Z2	nd	0.01	1.59	nd	nd
27	AA2	nd	0.01	1.65	nd	nd
28	AB2	nd	0.01	1.46	nd	nd
29	AC2	0.08		4.28	0.00	0.00
30	AD2	nd		3.64	0.01	< 0.05
31	AE2	nd		3.63	nd	< 0.05
32	RW: 1	0.06		10.54	0.02	0.02
33	RW: 2	0.06		10.54	0.02	0.02
34	RW: 3	nd		14.03	nd	nd
35	RW: 4	nd		14.03	nd	nd

Table A.40: Comparison of calculated diffusion coefficients using Eq. 5.2 to values obtained from literature

Molecule	Literature (m^2/s)	Reference	Calculated* (m^2/s)	Error (%)
Na	1.33E-09	Baştuğ and Kuyacak (2005)	1.25E-09	6
K	1.96E-09	Baştuğ and Kuyacak (2005)	1.00E-09	49
Ca	7.90E-09	Baştuğ and Kuyacak (2005)	9.90E-10	-25
Cd	6.80E-10	Furukawa and Takahashi (2008)	6.52E-10	4
La	6.23E-10	Furukawa and Takahashi (2008)	5.98E-10	4
Eu	6.06E-10	Furukawa and Takahashi (2008)	5.75E-10	5
Ce	6.09E-10	Furukawa and Takahashi (2008)	5.95E-10	2
$Fe(CN)_6^{3-}$	7.17E-10	Baur and Wightman (1990)	5.03E-10	30
$Ru(NH)_6^{3+}$	5.48E-10	Baur and Wightman (1990)	5.24E-10	4
Average				**14**
$Pt(CN)_4^{2-}$			4.36E-10	

*Eq. 5.2 (Grunwald, 1989)

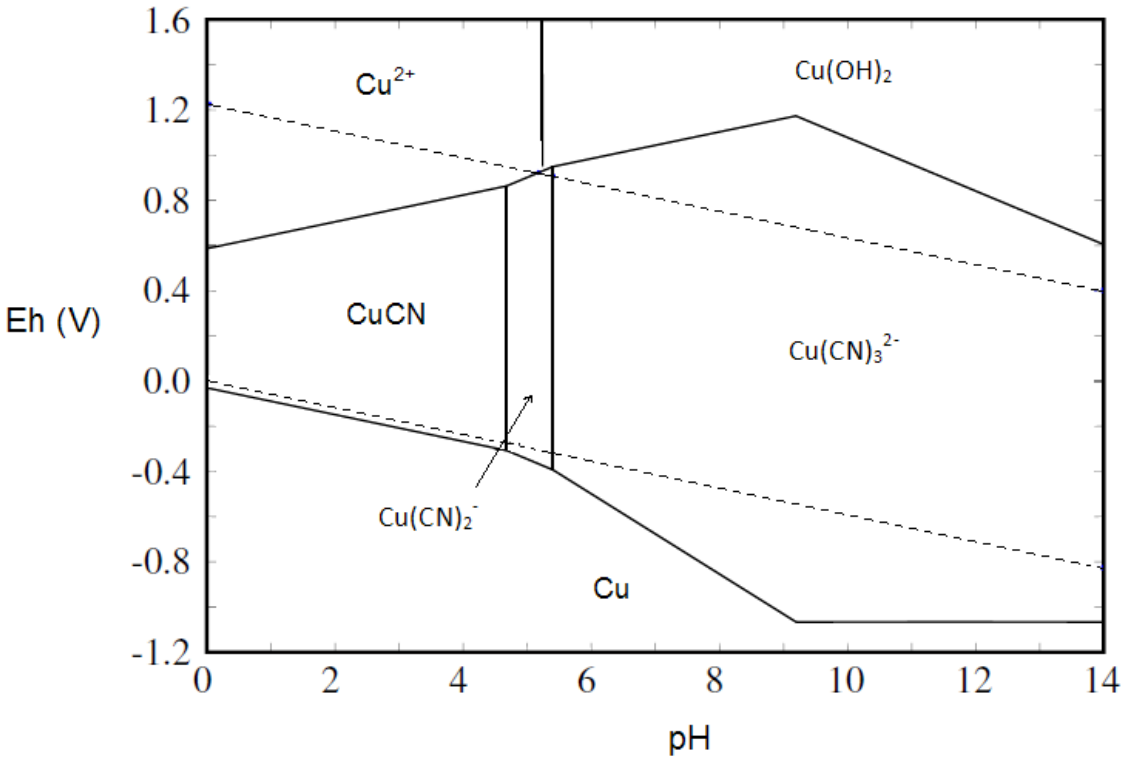


Figure A.141: Eh-pH diagram for the Cu-CN-H_2O system at 25°C (re-drawn from Souza et al. 2014)

Activated Carbon specifications

Marlyn Chemicals
(Pty) Ltd
Reg No. 90/ 01843/ 07

PO Box 39428
Booysens 2016
Johannesburg
South Africa

Tel : (011) 436-0683/4/5 National
Tel : +27 11 436-0683/4/5 International
Fax : 436-0705
e-mail: marlyn@cybertrade.co.za

MC 110 High Activity Coconut Based Activated Carbon

Parameters	Value	Test Method
Surface Area (m^2/g)	1200	BET N_2
Iodine Value (mg/g)	1050 – 1100	SSC 206
CTC Adsorption	65	ASTM D3467
Bulk Density (g/cm^3)	0.49-0.52	ASTM D2854
Ash Content (%)	2.5-3.0	ASTM D2866
Hardness (%) minimum	98	ASTM D3802
Moisture (%) as packed	2	SSC 57
PH of H_2O extract	10	ASTM D3838
Water soluble matter (%)	<1	SSC 54
K Value	26	AARL
R Value	60	AARL
ARF (%) minimum	80	SSC

Marlyn Gold Carbons are produced under strict controlled conditions to ensure the highest levels of quality. Selected coconut chars are gently steam activated in rotary kilns to ensure consistent production of a hard, naturally pre-attritioned activated carbon that exhibits rapid adsorbtion kinetics, high loading capacities and consistent performance in circuit.

This product is available in a variety of mesh sizes to ASTM D2867. The most commonly used sizes and packaging in the Gold Industry are:

USS 6x12	**(3.35mm – 1.7mm)**	**25kg/500kg bags**
USS 8x16	**(2.36mm – 1.18mm)**	**25kg/500kg bags**

Director: L R Palmer

Appendix B

Experimental data

Adsorption experiments data

Isotherm data

Table B.41: Adsorption analysis data for the development of a Pt Isotherm. (Temperature - 25°C, rolling bottle method)

Solution amount (l)	0.5			
		Analysis ICP –OES (mg/L)		Calculated
	Activated Carbon (g)	Na	Pt	Loading (mg/g)
30mg/L base		1226	36.41	
70mg/L base		1251	82.53	
Pt 0.6g/L AC 30mg/L	0.3	1167	17.64	31.28
Pt 1g/L AC 30mg/L	0.5	1211	11.96	24.45
2g/L AC 30mg/L	1.0	1215	1.33	17.54
Pt 3g/L AC 30mg/L	1.5	735	0.06	12.12
Pt 4g/L AC 30mg/L	2.0	1219	0.26	9.04
Pt 0.6g/L 70mg/L	0.3	1328	56.66	43.12
Pt 1g/L AC 70mg/L	0.5	1263	45.72	36.81
Pt 2g/L AC 70mg/L	1.0	1223	23.11	29.71
Pt 3g/L AC 70mg/L	1.5	1300	7.93	24.87
Pt 4g/L AC 70mg/L	2.0	863	0.77	20.44

Table B.42: Adsorption analysis data for the development of a Pt Isotherm. (Temperature - 25°C, rolling bottle method)

Solution amount (l)	0.5			
		Analysis ICP –OES (mg/L)		Calculated
	Activated Carbon weight (g)	Na	Pt	Loading (mg/g)
Pd base 30mg/L		1221	29.84	
Pd base 64mg/L		851.8	63.62	
Pd 0.6g/L 30mg/L	0.3	1259	19.70	16.90
Pd 1g/L 30mg/L	0.5	1264	14.40	15.44
Pd 2g/L 30mg/L	1.0	1246	5.97	11.94
Pd 3g/L 30mg/L	1.5	801.2	0.37	9.82
Pd 4g/L 30mg/L	2.0	1222	0.53	7.33
Pd 0.6g/L 64mg/L	0.3	910.1	49.19	24.05
Pd 1g/L 64mg/L	0.5	925.5	41.82	21.80
Pd 2g/L 64mg/L	1.0	837.1	26.61	18.51
Pd 3g/L 64mg/L	1.5	941.2	12.82	16.93
Pd 4g/L 64mg/L	2.0	978.4	5.60	14.51

Temperature loading experiments

Table B.43: Adsorption analysis for Pt, Pd and Au at 25°C in a stirred vessel (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs)

		Analysis - ICP MS (mg/L)				Calculation		
	Time (hrs)	Na	Pd	Pt	Au	Pd (%)	Pt (%)	Au %)
LT 25:1	0.000	399.00	0.854	0.787	0.303	0	0	0
LT 25:2	0.250	413.00	0.309	0.270	0.008	64	66	97
LT 25:3	0.500	405.60	0.101	0.084	0.000	88	89	100
LT 25:4	1.000	397.10	0.014	0.010	0.000	98	99	100
LT 25:5	1.500	399.40	0.002	0.001	0.000	100	100	100
LT 25:6	2.000	396.50	0.000	0.000	0.000	100	100	100
LT 25:7	3.000	401.20	0.000	0.000	0.000	100	100	100

Table B.44: Adsorption analysis for Pt, Pd and Au at 35°C in a stirred vessel (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs)

		Analysis - ICP MS (mg/L)				Calculation		
	Time (hrs)	Na	Pd	Pt	Au	Pd (%)	Pt (%)	Au %)
LT 35:1	0.000	406.60	0.914	0.821	0.309	0	0	0
LT 35:2	0.250	396.40	0.216	0.184	0.003	76	78	99
LT 35:3	0.500	397.90	0.059	0.049	0.000	94	94	100
LT 35:4	1.000	404.20	0.005	0.004	0.005	99	99	98
LT 35:5	1.500	409.20	0.001	0.001	0.001	100	100	100
LT 35:6	2.000	408.80	0.000	0.000	0.001	100	100	100
LT 35:7	3.000	401.10	0.000	0.000	0.000	100	100	100

Table B.45: Adsorption analysis for Pt, Pd and Au at 50°C in a stirred vessel (pH = 9.5, BM = 0, CN = 0, AC = 10 g/L, PGMs)

		Analysis - ICP MS (mg/L)				Calculation		
	Time (hrs)	Na	Pd	Pt	Au	Pd (%)	Pt (%)	Au %)
LT 50:1	0.000	407.90	0.919	0.819	0.310	0	0	0
LT 50:2	0.250	413.10	0.180	0.151	0.001	80	82	100
LT 50:3	0.500	413.30	0.038	0.031	0.000	96	96	100
LT 50:4	1.000	420.20	0.006	0.004	0.000	99	100	100
LT 50:5	1.500	420.30	0.004	0.003	0.000	100	100	100
LT 50:6	2.000	407.20	0.003	0.002	0.000	100	100	100
LT 50:7	3.000	410.30	0.003	0.002	0.000	100	100	100

Consecutive loading experiment nr 1 - (CN = 0, BM = 0, Temperature = 25°C)

Table B.46: Consecutive loading 1 - PGM adsorption analysis after 4 consecutive loadings (CN = 0, BM = 0, Temperature = 25°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR1 000D	0.0444	nd	0.1468	1.0053	0.2170
1	AHR1 120D	0.0215	nd	0.0003	0.0034	0.0007
2	AHR1 240D	0.0159	nd	0.0005	0.0046	0.0008
3	AHR1 360D	0.0211	nd	0.0008	0.0057	0.0011
4	AHR1 480D	0.0389	0.0018	0.0011	0.0077	0.0012

Table B.47: Consecutive loading 1 - PGM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 0, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0	-	0	-	0
1	99.8	24.9	99.7	24.9	99.7	24.9
2	99.7	49.9	99.5	49.8	99.6	49.8
3	99.4	74.7	99.4	74.7	99.5	74.7
4	99.2	99.5	99.2	99.5	99.4	99.6

Consecutive loading experiment nr 2 - (CN = 0, BM = 20, Temperature = 50°C)

Table B.48: Consecutive loading 2 - PGM adsorption analysis after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 50°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR2 000	5.5940	7.9260	1.0244	0.9963	0.2312
1	AHR2 120	0.1399	0.7292	0.0371	0.0266	0.0008
2	AHR2 240	0.5464	2.7650	0.1703	0.1214	0.0022
3	AHR2 360	1.0090	4.4860	0.3241	0.2296	0.0039
4	AHR2 480	2.2490	5.4470	0.4436	0.3182	0.0055

Table B.49: Consecutive loading 2 - PGM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0.0	-	0.0	-	0.0
1	96.4	24.1	97.3	24.3	99.7	24.9
2	83.4	44.9	87.8	46.3	99.1	49.7
3	68.4	62.0	77.0	65.5	98.3	74.3
4	56.7	76.2	68.1	82.5	97.6	98.7

Table B.50: Consecutive loading 2 - BM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated BM adsorption (%)			
Contact	Cu (%/contact)	Cu (Total cum %)	Ni (%/contact)	Ni (Total cum %)
Base	-	0	-	0
1	97.5	24.4	90.8	22.7
2	90.2	46.9	65.1	39.0
3	82.0	67.4	43.4	49.8
4	59.8	82.4	31.3	57.6

Consecutive loading experiment nr 3 - (CN = 0, BM = 20, Temperature = 25°C)

Table B.51: Consecutive loading 3 - PGM adsorption analysis after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR3 000	4.4850	7.6110	0.1552	1.0871	0.2233
1	AHR3 120	0.7732	0.2809	0.0017	0.0150	0.0001
2	AHR3 240	1.5030	0.9286	0.0070	0.0418	0.0009
3	AHR3 360	1.5780	1.5960	0.0135	0.0834	0.0020
4	AHR3 480	1.6440	2.2260	0.0215	0.1282	0.0031

Table B.52: Consecutive loading 3 - PGM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0.0	-	0.0	-	0.0
1	98.9	24.7	98.6	24.7	100.0	25.0
2	95.5	48.6	96.2	48.7	99.6	49.9
3	91.3	71.4	92.3	71.8	99.1	74.7
4	86.2	93.0	88.2	93.8	98.6	99.3

Table B.53: Consecutive loading 3 - BM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated BM adsorption (%)			
Contact	Cu (%/contact)	Cu (Total cum %)	Ni (%/contact)	Ni (Total cum %)
Base	-	0.0	-	0.0
1	82.8	20.7	96.3	24.1
2	66.5	37.3	87.8	46.0
3	64.8	53.5	79.0	65.8
4	63.3	69.4	70.8	83.5

Consecutive loading experiment nr 4 - (CN = 0, BM = 0, Temperature = 50°C)

Table B.54: Consecutive loading 4 - PGM adsorption analysis after 4 consecutive loadings (CN = 0, BM = 0, Temperature = 50°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR4 000	0.0762	nd	0.1290	0.8205	0.1600
1	AHR4 120	0.0354	nd	0.0048	0.0264	0.0006
2	AHR4 240	0.0410	nd	0.0117	0.0630	0.0013
3	AHR4 360	0.0730	nd	0.0165	0.0955	0.0019
4	AHR4 480	0.1129	nd	0.0218	0.1250	0.0027

Table B.55: Consecutive loading 4 - PGM adsorption calculation after 4 consecutive loadings (CN = 0, BM = 0, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0.0	-	0.0	-	0.0
1	96.3	24.1	96.8	24.2	99.6	24.9
2	91.0	46.8	92.3	47.3	99.2	49.7
3	87.2	68.6	88.4	69.4	98.8	74.4
4	83.1	89.4	84.8	90.6	98.3	99.0

Consecutive loading experiment nr 5 - (CN = 300, BM = 20, Temperature = 25°C)

Table B.56: Consecutive loading 5 - PGM adsorption analysis after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR5 000	10.8500	8.0120	0.1534	0.9450	0.2074
1	AHR5 120	10.0200	1.6880	0.0124	0.0666	0.0017
2	AHR5 240	10.7400	3.5070	0.0281	0.1572	0.0027
3	AHR5 360	10.7800	4.5960	0.0409	0.2286	0.0040
4	AHR5 480	11.0200	0.7278	0.0503	0.2835	0.0051

Table B.57: Consecutive loading 5 - PGM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0.0	-	0.0	-	0.0
1	91.9	23.0	93.0	23.2	99.2	24.8
2	81.7	43.4	83.4	44.1	98.7	49.5
3	73.3	61.7	75.8	63.0	98.1	74.0
4	67.2	78.6	70.0	80.5	97.6	98.4

Table B.58: Consecutive loading 5 - BM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated BM adsorption (%)			
Contact	Cu (%/contact)	Cu (Total cum %)	Ni (%/contact)	Ni (Total cum %)
Base	-	0.0	-	0.0
1	7.6	1.9	78.9	19.7
2	1.0	2.2	56.2	33.8
3	0.6	2.3	42.6	44.4
4	0.0	2.3	90.9	67.2

Consecutive loading experiment nr 6 - (CN = 300, BM = 0, Temperature = 50°C)

Table B.59: Consecutive loading 6 - PGM adsorption analysis after 4 consecutive loadings (CN = 300, BM = 0, Temperature = 50°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR6 000	0.4881	0.1126	0.1538	1.0038	0.2201
1	AHR6 120	0.7532	0.2633	0.0214	0.1280	0.0022
2	AHR6 240	0.5750	0.3150	0.0393	0.2415	0.0041
3	AHR6 360	0.6926	0.2898	0.0538	0.3346	0.0056
4	AHR6 480	0.5035	0.2230	0.0638	0.4083	0.0076

Table B.60: Consecutive loading 6 - PGM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 0, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0	-	0	-	0
1	86.1	21.5	87.2	21.8	99.0	24.7
2	74.5	40.1	75.9	40.8	98.1	49.3
3	65.0	56.4	66.7	57.5	97.5	73.7
4	58.6	71.0	59.3	72.3	96.5	97.8

Consecutive loading experiment nr 7 - (CN = 300, BM = 0, Temperature = 25°C)

Table B.61: Consecutive loading 7 - PGM adsorption analysis after 4 consecutive loadings (CN = 300, BM = 0, Temperature = 25°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR7 000	0.0601	nd	0.1714	1.2664	0.2604
1	AHR7 120	0.1080	nd	0.0028	0.0252	0.0009
2	AHR7 240	1.3530	0.0875	0.0069	0.0507	0.0014
3	AHR7 360	1.2260	0.1275	0.0100	0.0703	0.0017
4	AHR7 480	0.8922	0.1741	0.0150	0.0865	0.0035

Table B.62: Consecutive loading 7 - PGM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 0, Temperature = 25°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0	-	0	-	0
1	98.4	24.6	98.0	24.5	99.7	24.9
2	96.0	48.6	96.0	48.5	99.4	49.8
3	94.2	72.1	94.4	72.1	99.3	74.6
4	91.3	94.9	93.2	95.4	98.7	99.3

Consecutive loading experiment nr 8 - (CN = 300, BM = 20, Temperature = 50°C)

Table B.63: Consecutive loading 8 - PGM adsorption analysis after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 25°C, pH = 9.5, stirred vessel)

		Analysis ICP -MS (mg/L)				
Contact	Sample	Cu	Ni	Pd	Pt	Au
Base	AHR8 000	10.4000	8.1030	0.1613	1.0642	0.2360
1	AHR8 120	10.2100	3.2390	0.0276	0.1803	0.0043
2	AHR8 240	10.6300	5.4380	0.0579	0.3970	0.0083
3	AHR8 360	10.5700	6.3290	0.0752	0.5200	0.0126
4	AHR8 480	10.3900	6.9530	0.0983	0.6730	0.0256

Table B.64: Consecutive loading 8 - PGM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated adsorption (%)					
Contact	Pd (%/contact)	Pd (Total cum %)	Pt (%/contact)	Pt (Total cum %)	Au (%/contact)	Au (Total cum %)
Base	-	0.0	-	0.0	-	0.0
1	82.9	20.7	83.1	20.8	98.2	24.5
2	62.2	36.7	62.7	36.4	96.5	48.7
3	51.0	50.1	51.1	49.2	94.7	72.3
4	35.9	59.9	36.8	58.4	89.2	94.6

Table B.65: Consecutive loading 8 - BM adsorption calculation after 4 consecutive loadings (CN = 300, BM = 20, Temperature = 50°C, pH = 9.5, stirred vessel)

	Calculated BM adsorption (%)			
Contact	Cu (%/contact)	Cu (Total cum %)	Ni (%/contact)	Ni (Total cum %)
Base	-	0	-	0
1	1.8	0.5	60.0	15.0
2	0.0	0.5	32.9	23.2
3	0.0	0.5	21.9	28.7
4	0.1	0.5	14.2	32.3

Loading for elution

Table B.66: Sample analysis and loading details for the first loading procedure for elutions B,C,D,E

Loading for experiment	B,C,D,E
Volume (l)	4
AC (g/L)	8
time (hr)	65
Loading procedure*	1

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**	0.98	0.97	0.97		
	Measured	0.95	0.93	1.16		
	Error (%)	3.00	3.80	19.38		
Time (hr)	**Sample**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
0	MZ0	6.24	0.00	620.70	5.81	5.54
65	NB1	< 0.001	0.00	506.3	0.02	< 0.001

Table B.67: Sample analysis and loading details for loading A for elutions F and G. Effect of Cu

Loading for experiment	F,G
Volume (l)	2
AC (g/L)	8
time (hr)	65
NaCN (mg/L)	30
Loading procedure[1]	2

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**	0.98	0.97	0.97		
	Measured	0.95	0.93	1.16		
	Error (%)	3.00	3.80	19.38		
Time (hr)	**Sample**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
0	L:A0	5.61	42.86	437.00	4.94	5.01
1	L:A1	0.45	42.27	433.00	1.91	1.81
65	L:A2	< 0.001	0.28	447.60	0.10	0.22

* As per Table 3.6 in Chapter 3

Table B.68: Sample analysis and loading details for loading B for elutions I and J. Effect of KSCN and Cu.

Loading for experiment	I,J
Volume (l)	2
AC (g/L)	8
time (hr)	65
KSCN	100
NaCN (mg/L)	30
Loading procedure[1]	3

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**	0.89	0.97	0.97		
	Measured	0.98	1.02	0.96		
	Error (%)	10.35	4.85	0.96		
Time (hr)	**Sample**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
0	L:B0	4.47	40.30	458.10	2.48	2.66
1	L:B1	0.23	21.82	130.40	0.50	0.48
65	L:B2	0.08	145.10	1864.00	0.33	0.25

Table B.69: Sample analysis and loading details for loading C for elutions K,L,M,N

Loading for experiment	K,L,M,N
Volume (l)	4
AC (g/L)	8
time (hr)	65
Loading procedure[1]	1

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**	0.92	9.20	9.20		
	Measured	1.00	9.29	9.47		
	Error (%)	8.80	0.99	2.97		
Time (hr)	**Sample**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
0	L:C0	5.01	nd	291.00	3.38	5.31
1	L:C1	nd	nd	302.00	nd	nd
65	L:C2	nd	nd	297.40	nd	nd

Table B.70: Sample analysis and loading details for loading D for elutions O – Z and AA - AE

Loading for experiment	O - Z, AA - AE
Volume (l)	16
AC (g/L)	8
time (hr)	65
Loading procedure[1]	1

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**					
	Measured	0.98	0.97	0.97		
	Error (%)	0.96	0.94	1.02		
		1.64	2.74	4.74		
Time l(hr)	**(mg/L)**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
0	L:D0	5.25	0.00	563.30	3.84	4.66
0	L:D1	5.33	0.00	555.00	3.89	4.68
0.5	L:D2	0.35	0.00	569.60	0.86	0.90
1	L:D3	0.11	nd	557.60	0.47	0.47
2	L:D4	0.01	0.01	534.90	0.11	0.10
24	L:D5	nd	0.00	541.20	0.02	0.02
65	L:D6	nd	0.00	544.10	0.02	0.02

Table B.71: Sample analysis and loading details for loading E for elutions AG – AJ. The effect of water quality elutions

Loading for experiment	AG - AJ
Volume (l)	4
AC (g/L)	8
time (hr)	65
Loading procedure[1]	1

		Analysis ICP-OES (mg/L)				
		Au	**Cu**	**Na**	**Pd**	**Pt**
Quality Control	**Cert std value**	0.96			0.96	0.96
	Measured	0.94			0.91	0.97
	Error (%)	1.81			4.92	0.88
Time (hr)	**(Sample)**	**Au**	Cu	**Na**	**Pd**	**Pt**
0	L:E1	5.44	-	661.70	4.19	4.58
65	L:E2	nd	-	661.70	nd	0.01

Table B.72: Sample analysis and loading details for loading F for elutions AL – AM. The single component gold elution.

Loading for experiment	AL - AM
Volume (l)	2
AC (g/L)	8
time (hr)	65
Loading procedure	5

		Analysis ICP-OES (mg/L)
		Au
Quality Control	**Cert std value**	1.00
	Measured	1.03
	Error (%)	3.00
time (hr)	**Sample**	**Au**
0	L:Au0	9.18
65	L:Au1	0.01

Table B.73: Sample analysis and loading details for loading G for elutions with acid treatment

Loading for experiment	ACID 1 -5
Volume (l)	4
AC (g/L)	8
time (hr)	65
Loading procedure	6

		Analysis ICP - OES					
		Au	**Na**	**Pd**	**Pt**	**Cu**	**Ni**
Quality Control	**Cert std value**	1.96	9.8				
	Analysed	1.91	11.78				
	% Error	2.40	20.20				
Sample	**(mg/L)**	**Au**	**Na**	**Pd**	**Pt**	**Cu**	**Ni**
at start	L:C0	6.67	507.7	4.06	4.75	75.81	90.54
after 65 hours	L:C1	0.09	493.5	0.89	0.76	80.39	45.81

Table B.74: Sample analysis and loading details for loading H for the elution a higher loading

Max Capacity loading	
Volume (l)	1.25
AC (g/L)	8
time (hr)	120
Loading procedure	4

				Solution concentration (mg/L)			
Date	**Time (actual)**	**Time (hr)**	**Sample**	**Au**	**Na**	**Pd**	**Pt**
22-Feb	12:00	0	L:T 1	5.51	2921.00	30.82	28.65
22-Feb	13:00	1	L:T 2	0.04	2921.00	10.46	7.82
22-Feb	14:30	2.5	L:T 3	0.00	2903.00	6.83	4.78
22-Feb	17:00	5	L:T 4	0.00	2913.00	4.70	3.17
23-Feb	10:30	22.5	L:T 5	0.00	2921.00	2.08	1.33
24-Feb	11:00	47	L:T 6	0.00	2919.00	1.82	1.17
27-Feb	09:00	117	L:T 7	0.00	2882.00	1.83	1.17

Table B.75: Sample analysis and loading details for loading I for repeat elution experiments

Loading for experiment	Repeat 1 - 4
Volume (l)	4
AC (g/L)	8
time (hr)	65
Loading procedure	1

		Analysis ICP-OES (mg/L)				
Sample	**(mg/L)**	**Au**	**Cu**	**Na**	**Pd**	**Pt**
at start	L:I1	9.39	-	259.25	5.11	6.01
65 hr	L:I2	0.01	-	450.50	0.05	0.47

Table B.76: Sample analysis and loading details for loading J for the steel column elution experiments

Loading for experiment	100,110,130°C
Volume (l)	16
AC (g/L)	8
time (hr)	65
Loading procedure	1

		Analysis ICP-OES (mg/L)		
Sample	**(mg/L)**	**Au**	**Pd**	**Pt**
at start	0L1	3.772	1.727	2.265
at start	0L2	3.754	1.721	2.253
at start	0L3	3.779	1.719	2.268
at start	0L4	3.767	1.713	2.264
65 hr	1L1	< 0.003	< 0.004	< 0.003
66 hr	1L2	< 0.003	< 0.004	< 0.003
67 hr	1L3	< 0.003	< 0.004	< 0.003
68 hr	1L4	< 0.003	< 0.004	< 0.003

Table B.77: Sample analysis and loading details for loading K for the steel column elution experiments

Loading for experiment	120°C
Volume (l)	16
AC (g/L)	8
time (hr)	65
Loading procedure	1

		Analysis ICP-OES (mg/L)		
Sample	**(mg/L)**	**Au**	**Pd**	**Pt**
at start	2L1	3.667	1.41	2.204
at start	2L2	3.672	1.421	2.204
65 hr	3L1	< 0.003	< 0.004	< 0.003
66 hr	3L2	< 0.003	< 0.004	< 0.003

Elution experiments data

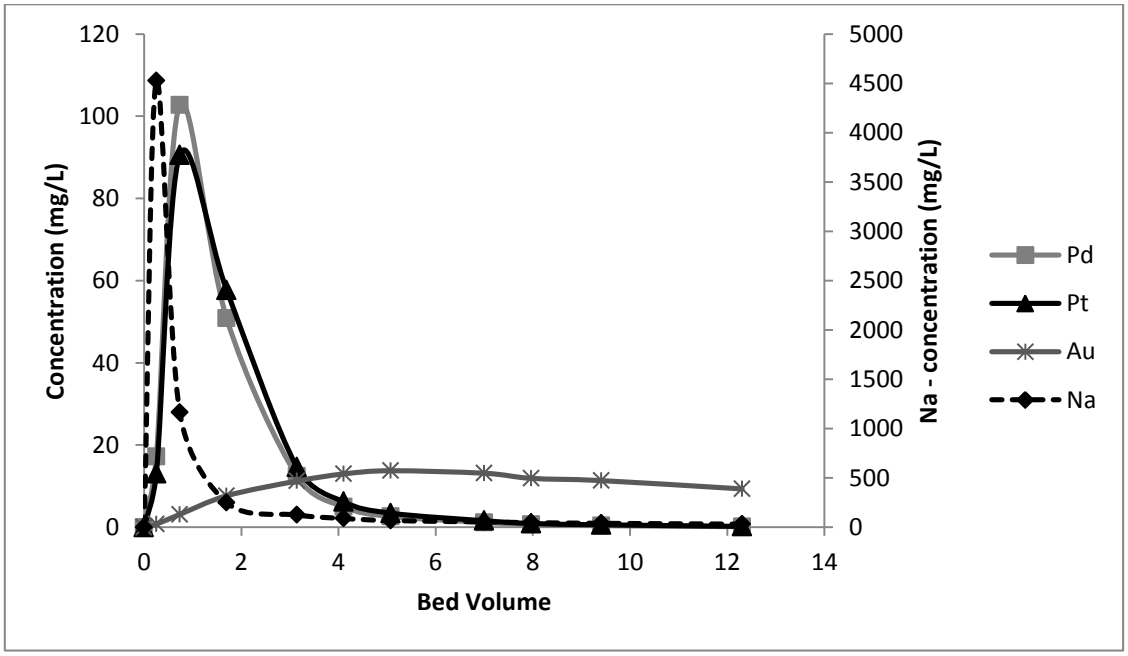
Elution experiment A

From carbon loading experiment 1

Date	
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.4
Activated Carbon (g)	12.92

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11.33
Flow rate (BV/hr)	3.2

Values in ppb (µg/L)					Na	Pd	Pt	Au
Quality Control	Sample Volume (mL)	Time	Sampling time (min)	Cert std value	20230			98
				Measured	18063			99
				Error (%)	11			1
Pre-treatment sample	10.3			NA1	13356071	43.1	24	<0.000
	6.4	12:52		NA2	4525379	17169.1	13094	760
	6.3	13:04	07:20	NA3	1162945	102722.4	90568	3122
	6.3	13:24		NA4	250472	50802.6	57725	7648
	6	13:51		NA5	124538	12415.6	14592	11240
	6.3	14:12		NA6	88769	4975.1	6182	12974
	6.3	14:35	9	NA7	67563	2609.4	3422	13747
	6.5	15:05	10	NA8	53913	1183.4	1585	13137
	6	15:34		NA9	46824	652.2	917	11892
	6.5	16:00		NA10	39918	404.8	594	11350
	6.5	17:03		NA11	31346	137.9	200	9323
	8.9	17:55		NA12	21824	25.2	33	5287
Bulk sample	10			NA13	373899	14184.0	14699	10036



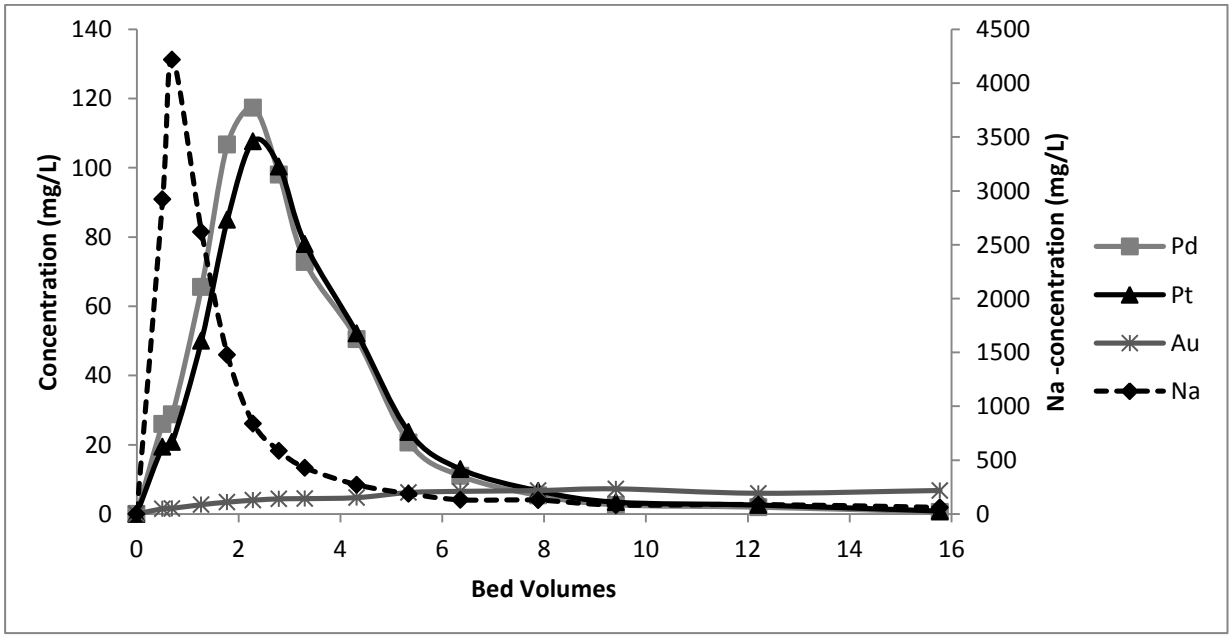
Elution experiment B

From carbon loading experiment 1

Date	07-Jul
Pre-treatment step	
NaOH (g)	0.8
NaCN (g)	0.11
Volume (mL)	40
Stirred (min)	30
pH	13.68
Activated Carbon (wet g)	13.03

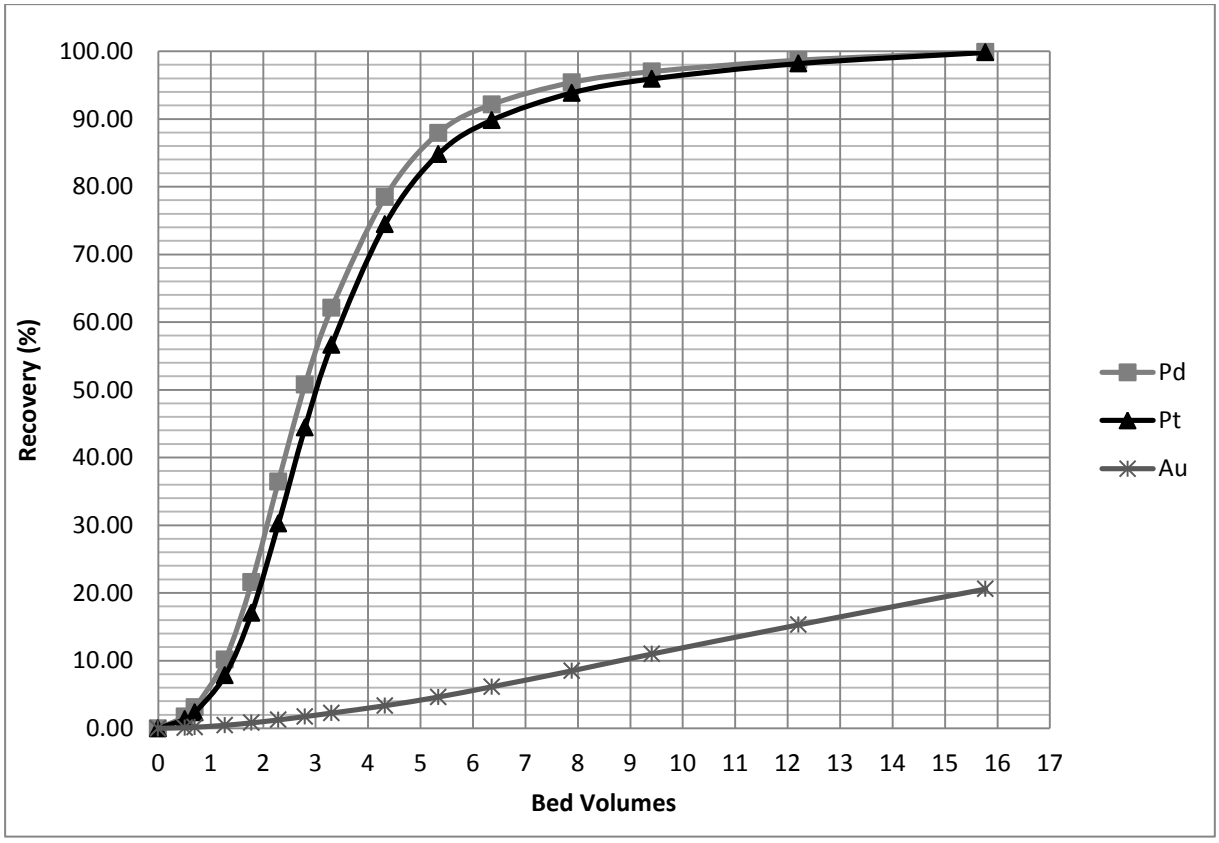
Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.8
Flow rate (BV/hr)	3.1

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	min	Flow rate (BV/hr)
sample after 65 hours adsorption	NB1	< 0.001	0.00	506.3	0.02	< 0.001					
Water	NB2	< 0.001	0.05	0.6	0.01	< 0.001					
Pre-treatment	NB3	-0.03	0.26	9241	0.12	< 0.001					
	NB4	1.53	1.13	2923.0	26.04	19.44	6.9		10:44		
	NB5	1.64	1.25	4220.0	28.77	20.81	7.2	10:44	10:53	9	3.43
	NB6	2.70	1.19	2621.0	65.55	50.05	6.5	10:53	11:01	8	3.48
	NB7	3.41	0.72	1479.0	106.70	85.00	6.6	11:01	11:11	10	2.83
	NB9	3.98	0.38	840.1	117.40	107.70	6.5	11:11	11:20	9	3.10
	NB8	4.38	0.21	586.6	98.06	100.40	6.5	11:20	11:29	9	3.10
	NB10	4.44	0.30	429.2	72.81	77.98	6.3	11:29	11:41	12	2.25
	NB11	4.72	0.10	271.10	50.52	52.17	6.6	11:51	12:00	9	3.14
	NB12	6.20	0.06	188.80	20.70	23.75	7.2	12:10	12:19	9	3.43
	NB13	6.54	0.05	131.70	11.00	12.95	6.8	12:32	12:42	10	2.91
	NB14	6.77	0.04	128.60	5.36	6.67	6.6	13:01	13:10	9	3.14
	NB15	7.27	0.03	82.79	2.66	3.42	6.5	13:32	13:40	8	3.48
	NB16	5.99	0.03	88.24	1.97	2.58	6.3	14:26	14:36	10	2.70
	NB17	6.79	0.03	61.50	0.60	0.85	6.3	15:34	15:44	10	2.70
Bulk sample	NB18	6.91	0.05	109.80	7.15	9.64	7				



Mass Balance	Initial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	dry AC (g)	PGM (mg)
Pt	5.54	4.00	22.16	8	0.69	6.9	4.78
Pd	5.81	4.00	23.23	8	0.73	6.9	5.01
Au	6.24	4.00	24.97	8	0.78	6.9	5.38

Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.09	0.00	0.06	0.00	0.01	0.00
6.62	0.51	0.07	1.73	0.05	1.33	0.00	0.09
9.10	0.70	0.35	3.10	0.26	2.36	0.02	0.16
16.54	1.27	0.57	10.14	0.45	7.81	0.02	0.43
23.15	1.78	0.74	21.57	0.64	17.04	0.02	0.79
29.77	2.29	0.71	36.45	0.69	30.22	0.03	1.21
36.38	2.80	0.57	50.75	0.59	44.44	0.03	1.69
43.00	3.31	0.82	62.10	0.86	56.64	0.06	2.19
56.23	4.33	0.47	78.47	0.50	74.43	0.07	3.24
69.46	5.34	0.21	87.93	0.24	84.81	0.08	4.49
82.69	6.36	0.16	92.14	0.19	89.83	0.13	5.95
102.53	7.89	0.08	95.40	0.10	93.85	0.14	8.23
122.38	9.41	0.08	97.00	0.11	95.92	0.24	10.64
158.76	12.21	0.06	98.68	0.08	98.18	0.30	14.82
205.07	15.77	0.01	99.88	0.01	99.82	0.07	19.94
225.35	17.33						
Sum		**4.98**		**4.84**		**1.22**	



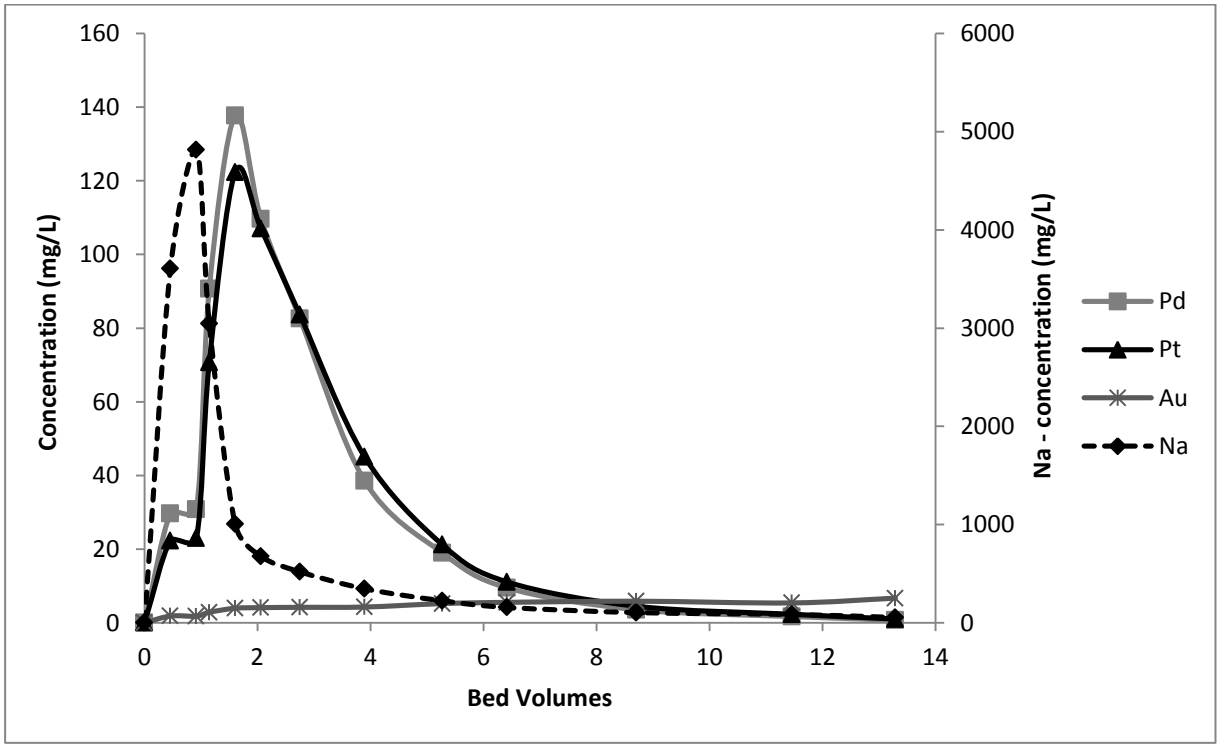
Elution experiment C

From carbon loading experiment 1

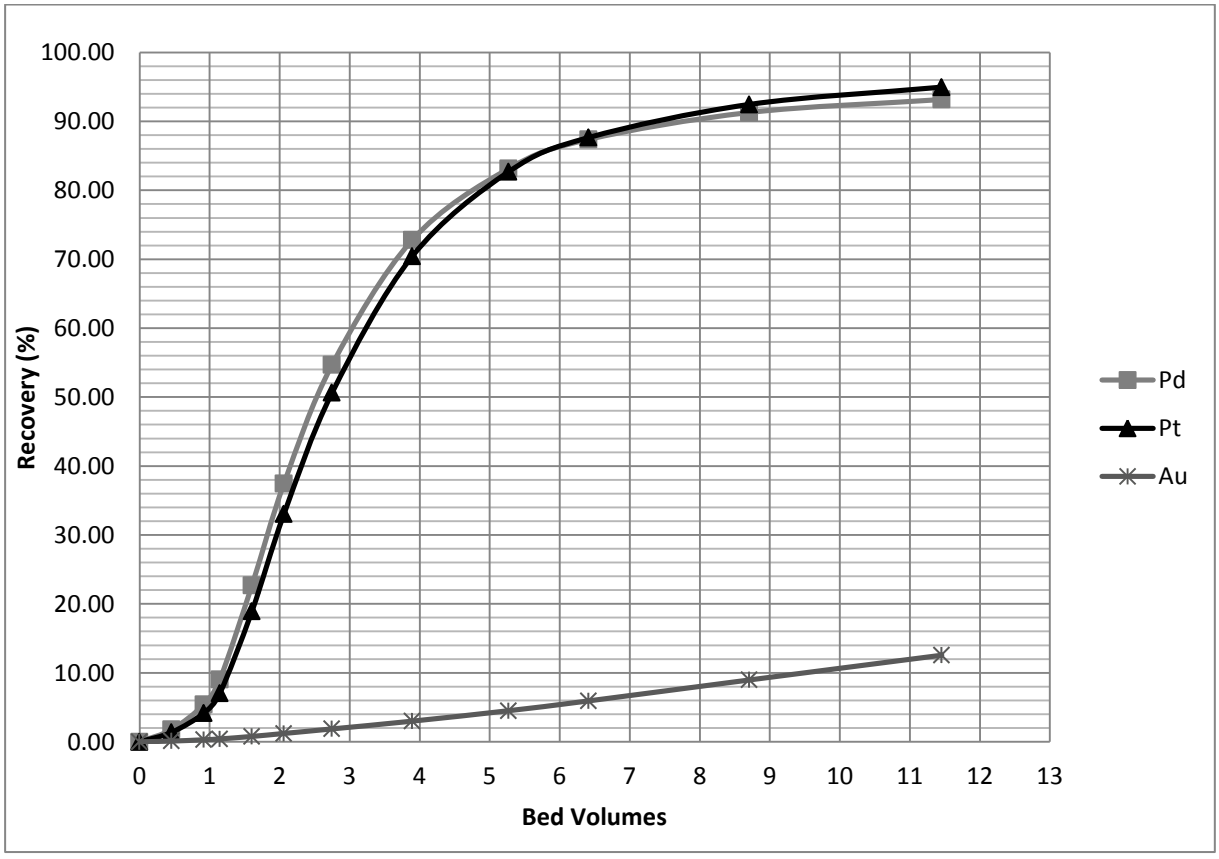
Date	07-Jul
Pre-treatment step	
NaOH (g)	0.8
NaCN (g)	0
Volume (mL)	40
Stirred (min)	30
pH	13.67
Activated Carbon (wet g)	12.04

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.95
Flow rate (BV/hr)	2.7

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NC1	0.03	0.08	10880.0	0.12	0.04					
water	NC2	0.00	0.07	0.7	< 0.001	< 0.001					
	NC3	1.83	0.11	3605.0	29.66	22.30	6.4	12:34	12:44	10	2.74
	NC4	1.78	0.08	4814	30.85	22.95	6.9	12:45	12:53	8	3.70
	NC5	2.86	0.04	3046.0	90.73	70.71	6.9	12:53	13:01	8	3.70
	NC6	3.94	0.03	1004.0	137.70	122.30	7.4	13:01	13:11	10	3.17
	NC7	4.11	0.02	677.4	109.60	107.00	6	13:11	13:21	10	2.57
	NC8	4.20	0.09	519.3	82.63	83.61	5.7	13:21	13:33	12	2.04
	NC9	4.28	0.01	346.4	38.55	45.07	6.5	13:50	14:01	11	2.53
	NC10	5.21	0.01	224.10	18.98	21.22	6.5	14:17	14:28	11	2.53
	NC11	5.54	0.00	156.60	9.49	11.09	5.5	14:45	14:55	10	2.36
	NC12	5.86	0.00	103.70	3.55	4.49	6.6	15:34	15:45	11	2.57
	NC13	5.39	0.00	84.88	1.70	2.31	6.1	16:32	16:44	12	2.18
	NC14	6.69	0.00	53.77	0.71	1.02	6.1	17:16	17:25	9	2.90
Bulk sample	NC15	5.86	0.22	100.50	8.81	11.76	6.9				



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.09	0.00	0.07	0.00	0.01	0.00
5.96	0.46	0.18	1.77	0.13	1.37	0.01	0.10
11.91	0.92	0.18	5.39	0.14	4.16	0.01	0.29
14.89	1.15	0.68	9.02	0.57	7.04	0.02	0.41
20.85	1.60	0.74	22.68	0.68	18.92	0.02	0.77
26.81	2.06	0.86	37.47	0.85	33.04	0.04	1.20
35.74	2.75	0.90	54.70	0.96	50.64	0.06	1.87
50.63	3.89	0.51	72.81	0.59	70.44	0.08	2.99
68.50	5.27	0.21	83.13	0.24	82.69	0.08	4.50
83.39	6.41	0.19	87.39	0.23	87.66	0.17	5.93
113.18	8.71	0.09	91.29	0.12	92.45	0.20	8.97
148.92	11.46	0.03	93.17	0.04	94.97	0.14	12.55
172.75	13.29						
Sum		**4.67**		**4.63**		**0.85**	



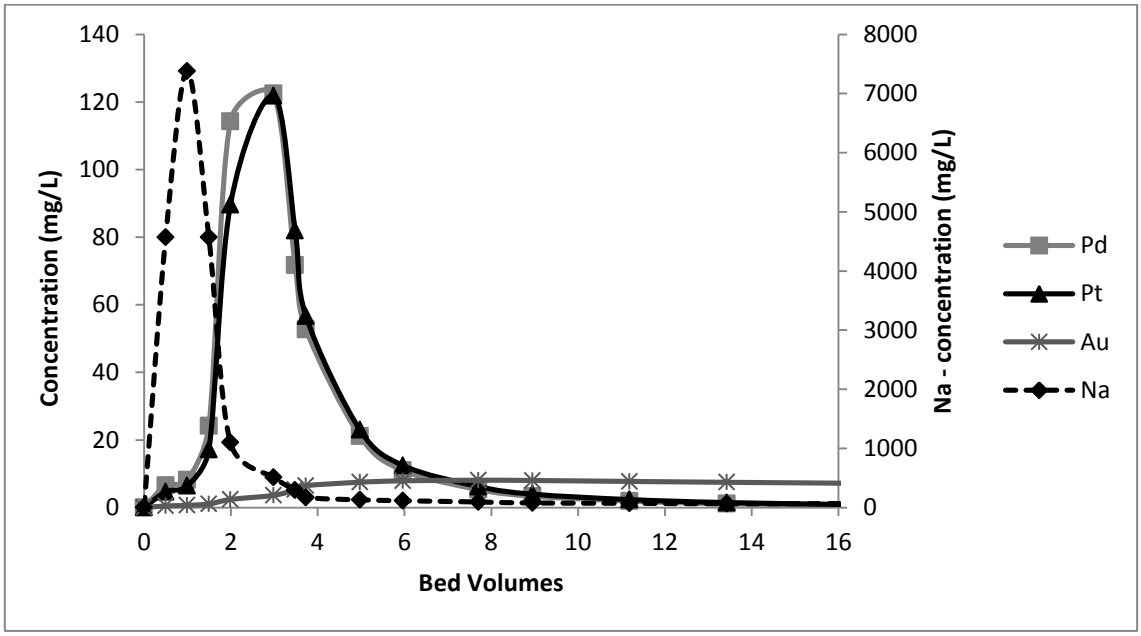
Elution experiment D

From carbon loading experiment 1

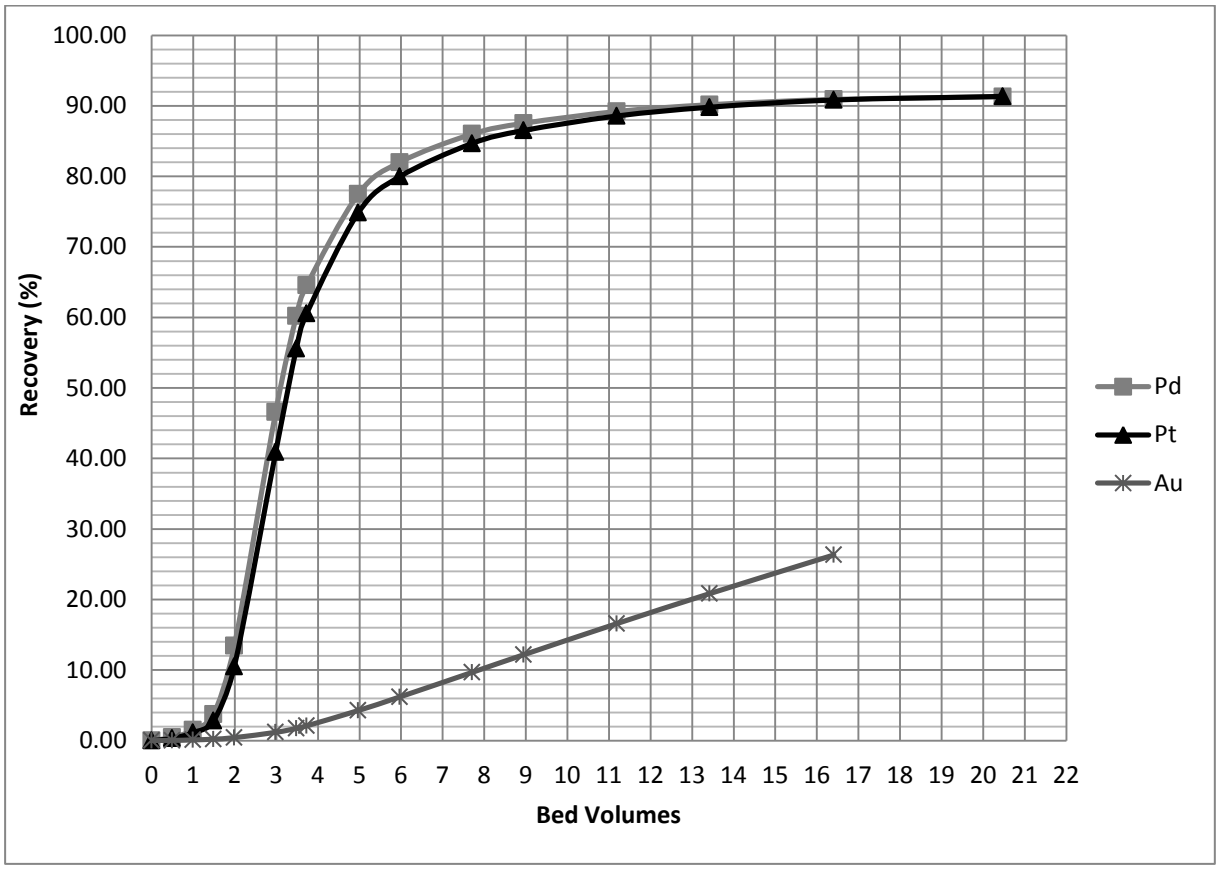
Date	08-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	12.87
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	60
Bed Volume (mL)	14
pH after	10.6
Flow rate (BV/hr)	3.0

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	ND1	0.19	0.43	10920	0.09	0.08					
water	ND2	< 0.001	0.03	0.6	< 0.001	< 0.001					
	ND3	0.49	0.70	4570.0	6.52	4.67	5.6	09:29	09:42	13	1.85
	ND4	0.67	0.98	7377.0	8.21	6.42	6.5	09:42	09:51	9	3.10
	ND5	1.07	1.05	4570.0	24.16	17.15	6.5	09:51	10:01	10	2.79
	ND6	2.40	0.78	1098.0	114.20	89.62	5.7	10:01	10:11	10	2.44
4 mL clear water spill into sample	ND7	1.72	0.28	339.3	79.83	71.91	8.4	10:11	10:23	12	3.00
	ND8	3.63	0.19	512.6	122.50	121.80	7.3	10:24			
	ND9	5.30	0.11	294.7	71.68	81.92	7				
	ND10	6.49	0.06	171.80	52.73	56.65	6.8	10:39	10:46	7	4.16
	ND11	7.51	0.04	131.10	21.17	23.00	6.9	11:00	11:08	8	3.70
	ND12	7.93	0.03	116.70	10.99	12.46	6.4	11:21	11:29	8	3.43
	ND13	8.10	0.03	94.76	5.35	6.23	7	11:54	12:03	9	3.33
	ND14	8.02	0.02	78.04	3.37	3.97	6.7	12:20	12:29	9	3.19
	ND15	7.74	0.02	73.04	1.92	2.37	6.5	13:02	13:13	11	2.53
	ND16	7.49	0.01	64.57	1.14	1.49	6.4	13:48	14:00	12	2.29
	ND17	7.19	0.01	68.74	0.66	0.87	6				
bulk sample	ND18	7.28	0.26	61.08	5.10	6.89	7				



Volume	BV	Pd	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.02	**0.00**	0.02	0.00	0.00	0.00
6.96	0.50	0.05	0.46	0.04	0.34	0.00	0.03
13.92	0.99	0.11	1.49	0.08	1.13	0.01	0.10
20.88	1.49	0.48	3.76	0.37	2.83	0.01	0.21
27.84	1.99	1.65	13.44	1.47	10.51	0.04	0.43
41.77	2.98	0.68	46.60	0.71	40.91	0.03	1.18
48.73	3.48	0.22	60.20	0.24	55.56	0.02	1.73
52.21	3.73	0.64	64.55	0.69	60.55	0.12	2.10
69.61	4.97	0.22	77.49	0.25	74.87	0.11	4.27
83.53	5.97	0.20	82.00	0.23	79.97	0.20	6.19
107.90	7.71	0.08	86.00	0.09	84.67	0.14	9.68
125.30	8.95	0.08	87.53	0.10	86.50	0.25	12.18
156.63	11.19	0.05	89.20	0.06	88.56	0.24	16.59
187.95	13.43	0.04	90.16	0.05	89.81	0.31	20.85
229.72	16.41	0.02	90.91	0.02	90.83		26.32
286.60	20.47		91.29		91.34		
Sum		**4.5369031**		**4.4209081**		**1.4741688**	



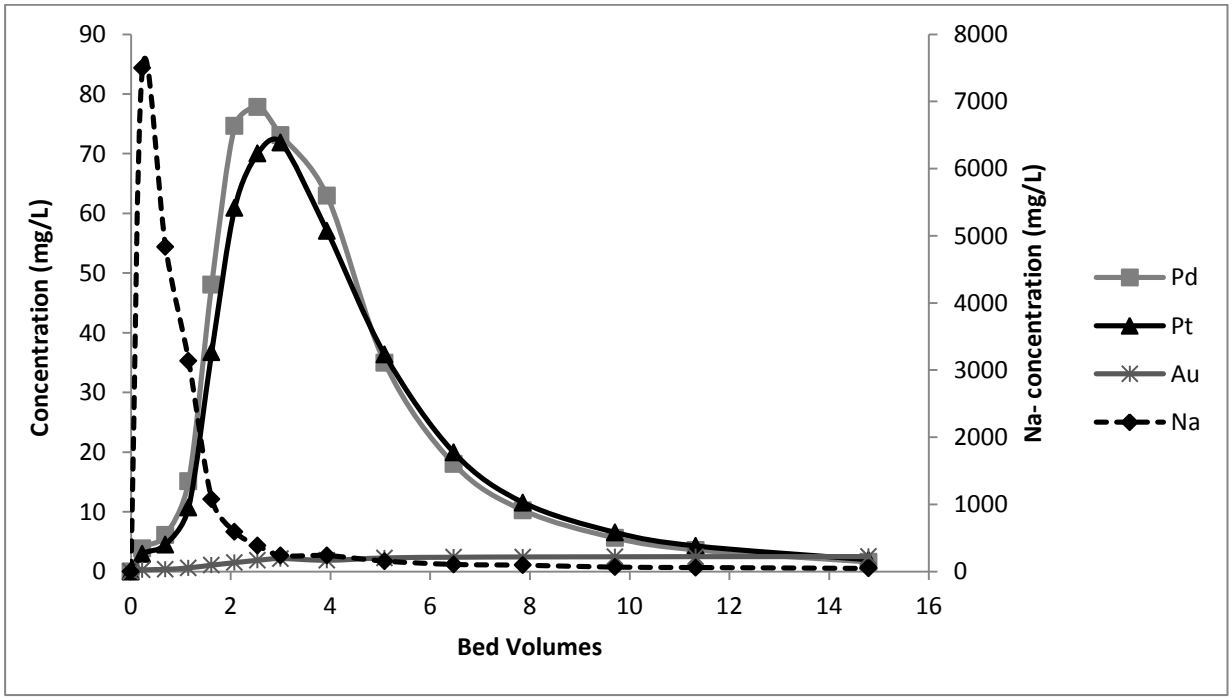
Elution experiment E

From carbon loading experiment 1

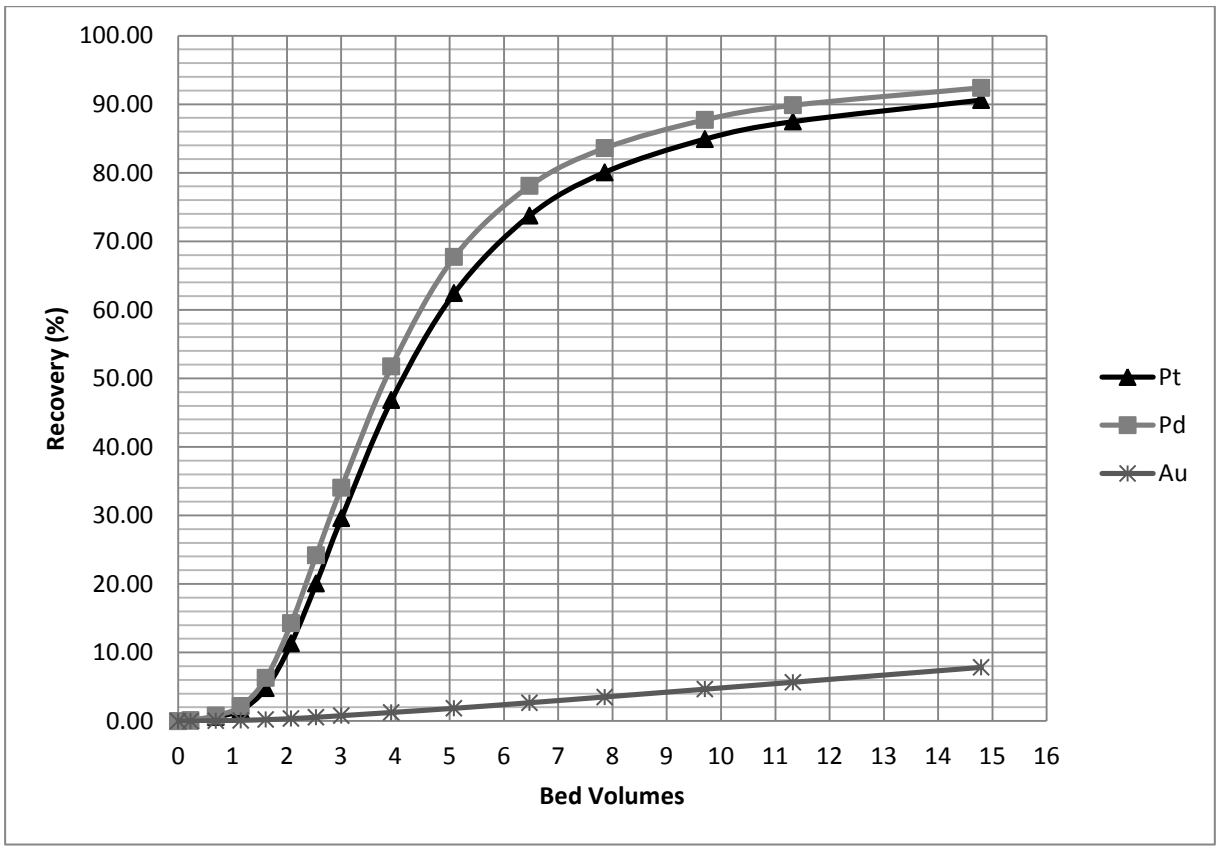
Date	08-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	1
Volume (mL)	40
Stirred (min)	30
pH	12.9
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	60
Bed Volume (mL)	14
pH after	10.55
Flow rate (BV/hr)	2.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NE1	< 0.001	0.30	7399	0.06	0.04					
water	NE2	< 0.001	0.04	0.6	< 0.001	< 0.001					
	NE3	0.28	0.88	7498.0	3.90	2.94	6.5	10:38	10:45	7	3.98
	NE4	0.36	0.77	4835.0	6.12	4.54	5.1	10:45	10:56	11	1.99
	NE5	0.62	0.95	3139.0	15.15	10.74	6.5	10:56	11:03	7	3.98
	NE6	1.07	0.64	1081.0	48.09	36.77	6	11:03	11:15	12	2.14
	NE7	1.50	0.34	591.1	74.64	60.91	6.6	11:15	11:25	10	2.83
	NE8	1.89	0.16	388.5	77.82	70.06	6.5	11:25	11:32	7	3.98
	NE9	2.18	0.11	238.40	73.13	71.89	5.4	11:32	11:43	11	2.10
	NE10	1.89	0.09	238.60	62.96	57.06	5.7	11:54	12:05	11	2.22
	NE11	2.29	0.06	155.70	35.00	36.37	6	12:21	12:30	9	2.86
	NE12	2.40	0.02	106.50	18.01	19.95	5.8	12:50	13:00	10	2.49
	NE13	2.45	0.02	94.57	10.27	11.57	5.8	13:22	13:32	10	2.49
	NE14	2.48	0.01	66.14	5.62	6.56	6.8	14:01	14:12	11	2.65
	NE15	2.50	0.01	60.34	3.63	4.29	6	14:37	14:47	10	2.57
	NE16	2.51	0.01	47.06	1.60	1.97	6	15:52	16:02	10	2.57
Bulk sample	NE17	2.63	0.03	68.68	10.52	13.35	6.8				



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
3.24	0.23	0.03	0.13	0.02	0.10	0.00	0.01
9.71	0.69	0.07	0.78	0.05	0.60	0.00	0.05
16.18	1.16	0.20	2.16	0.15	1.62	0.01	0.10
22.66	1.62	0.40	6.28	0.32	4.80	0.01	0.20
29.13	2.08	0.49	14.28	0.42	11.33	0.01	0.35
35.61	2.54	0.49	24.21	0.46	20.09	0.01	0.55
42.08	3.01	0.88	34.04	0.83	29.58	0.03	0.78
55.03	3.93	0.79	51.76	0.76	46.83	0.03	1.25
71.21	5.09	0.51	67.71	0.55	62.45	0.05	1.86
90.63	6.47	0.27	78.07	0.31	73.75	0.05	2.67
110.05	7.86	0.21	83.60	0.23	80.08	0.06	3.51
135.95	9.71	0.10	87.74	0.12	84.92	0.06	4.65
158.61	11.33	0.13	89.85	0.15	87.46	0.12	5.66
207.16	14.80		92.41		90.60		7.83
Sum		**4.593**		**4.385**		**0.438**	



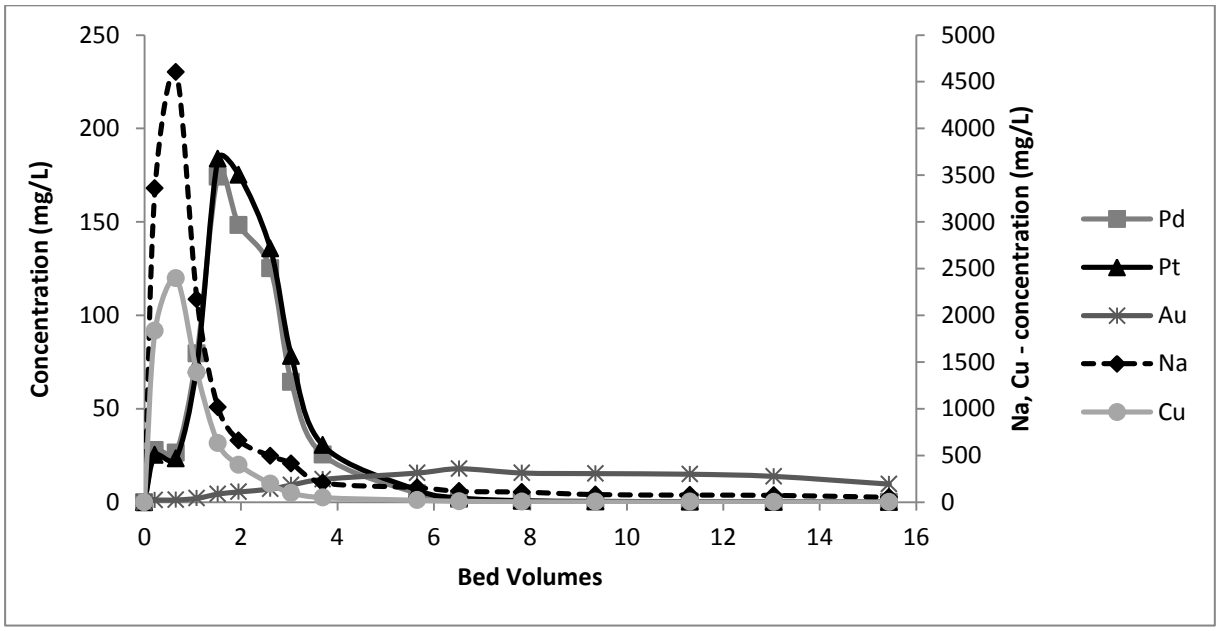
Elution experiment F

From carbon loading experiment A

Date	08-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.29
Activated Carbon (wet g)	12

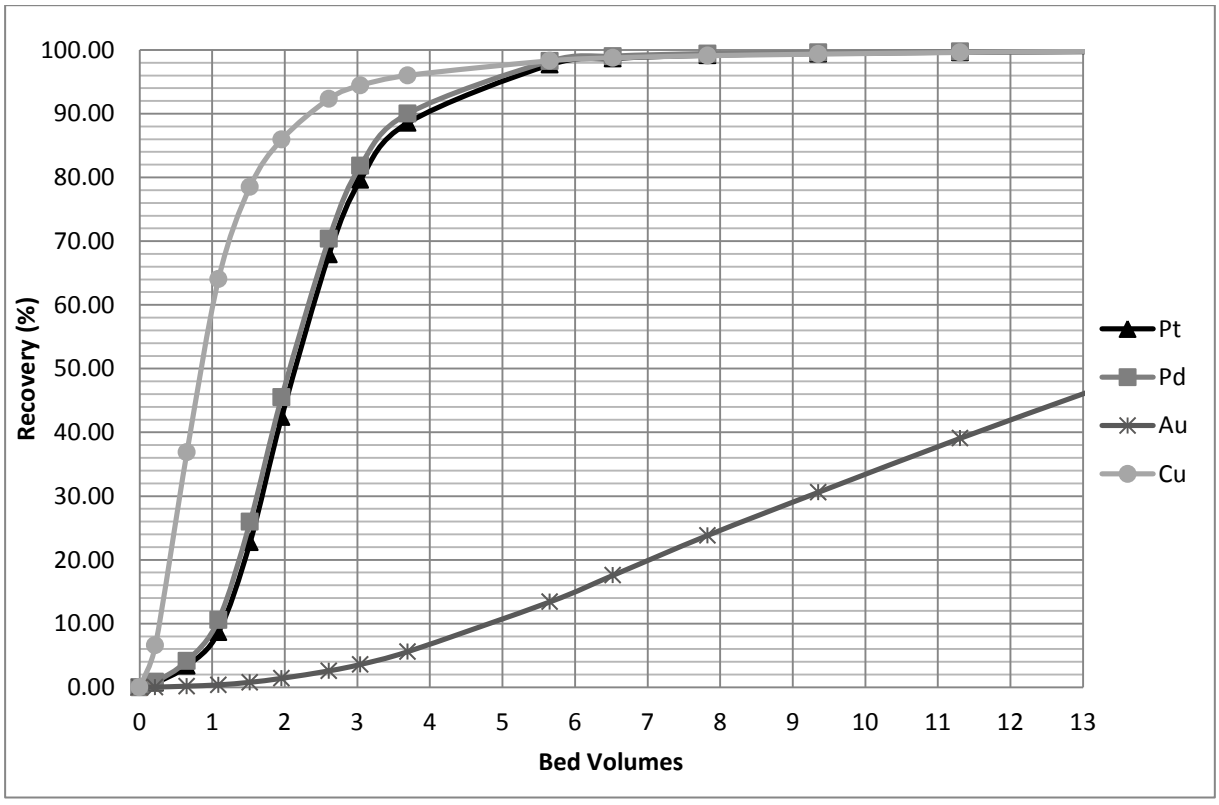
Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.28
Flow rate (BV/hr)	2.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NF1	0.02	952	10410	0.08	< 0.001					
water	NF2	0.00	4.89	4.34	< 0.001	< 0.001					
	NF3	1.10	1834.00	3360.0	27.87	25.35	6.5	09:32	09:42	10	2.79
	NF4	1.22	2396.00	4604.0	26.55	23.36	6.8	09:42	09:50	8	3.64
	NF5	2.09	1389.00	2170.0	79.58	73.47	7	09:50	09:57	7	4.29
	NF6	4.41	632.70	1017.0	174.10	183.70	5.9	09:57	10:10	13	1.95
	NF7	5.53	397.80	660.70	148.30	175.10	6	10:10	10:22	12	2.14
	NF8	7.07	197.10	495.4	125.10	135.70	5.8	10:22	10:34	12	2.07
	NF9	9.23	96.74	414.5	64.30	78.23	6.2	10:34	10:45	11	2.42
	NF10	12.27	49.29	208.90	25.42	30.53	5.4		11:02		
	NF11	15.65	21.60	156.20	4.78	6.47	6.7	11:37	11:46	9	3.19
	NF12	17.94	10.36	117.60	1.61	2.34	6.3	11:58	12:07	9	3.00
	NF13	15.67	5.48	108.50	0.56	0.85	6	12:29	12:38	9	2.86
	NF14	15.34	4.37	82.26	0.32	0.50	5.9	13:00	13:11	11	2.30
	NF15	15.00	3.67	76.98	0.18	0.30	6.4	13:44	13:56	12	2.29
	NF16	13.85	2.84	73.74	0.09	0.15	7.1	14:24	14:34	10	3.04
	NF17	9.72	1.25	53.42	0.05	0.07	6.9	15:20	15:29	9	3.29
Bulk sample	NF18	13.82	10.66	106.80	3.61	4.50	7				



Mass Balance	Inintial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	dry AC (g)	PGM (mg)
Pt	4.79	8.00	38.33	8	0.599	7.5	4.49
Pd	4.84	8.00	38.71	8	0.605	7.5	4.54
Au	5.61	8.00	44.90	8	0.70	7.5	5.26
Cu	42.86	8	342.88	8	5.36	7.5	40.18

Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)	Cu (mg)	Recovery (%)
0.00	0.00	0.04	**0.00**	0.04	0.00	0.00	0.00	2.79	0.00
3.05	0.22	0.17	0.84	0.15	0.69	0.01	0.03	12.88	6.58
9.14	0.65	0.32	4.14	0.29	3.36	0.01	0.18	11.53	36.91
15.23	1.09	0.77	10.58	0.78	8.66	0.02	0.38	6.16	64.05
21.32	1.52	0.98	25.96	1.09	22.75	0.03	0.79	3.14	78.55
27.41	1.96	1.25	45.51	1.42	42.39	0.06	1.41	2.72	85.94
36.54	2.61	0.58	70.38	0.65	67.92	0.05	2.58	0.89	92.34
42.63	3.05	0.41	81.86	0.50	79.64	0.10	3.59	0.67	94.44
51.77	3.70	0.41	90.03	0.51	88.57	0.38	5.60	0.97	96.01
79.17	5.66	0.04	98.27	0.05	97.69	0.20	13.41	0.19	98.30
91.35	6.53	0.02	99.04	0.03	98.66	0.31	17.58	0.14	98.76
109.62	7.83	0.01	99.44	0.01	99.18	0.33	23.85	0.10	99.10
130.94	9.35	0.01	99.62	0.01	99.44	0.42	30.59	0.11	99.35
158.35	11.31	0.00	99.76	0.01	99.64	0.35	39.08	0.08	99.61
182.71	13.05	0.00	99.83	0.00	99.74	0.39	46.25	0.07	99.79
216.20	15.44	0.01	99.87	0.01	99.81			0.02	
499.14	35.65			0.00	100.00				
563.36	40.24								
Sum		**5.02**		**5.56**		**2.66**		**42.47**	



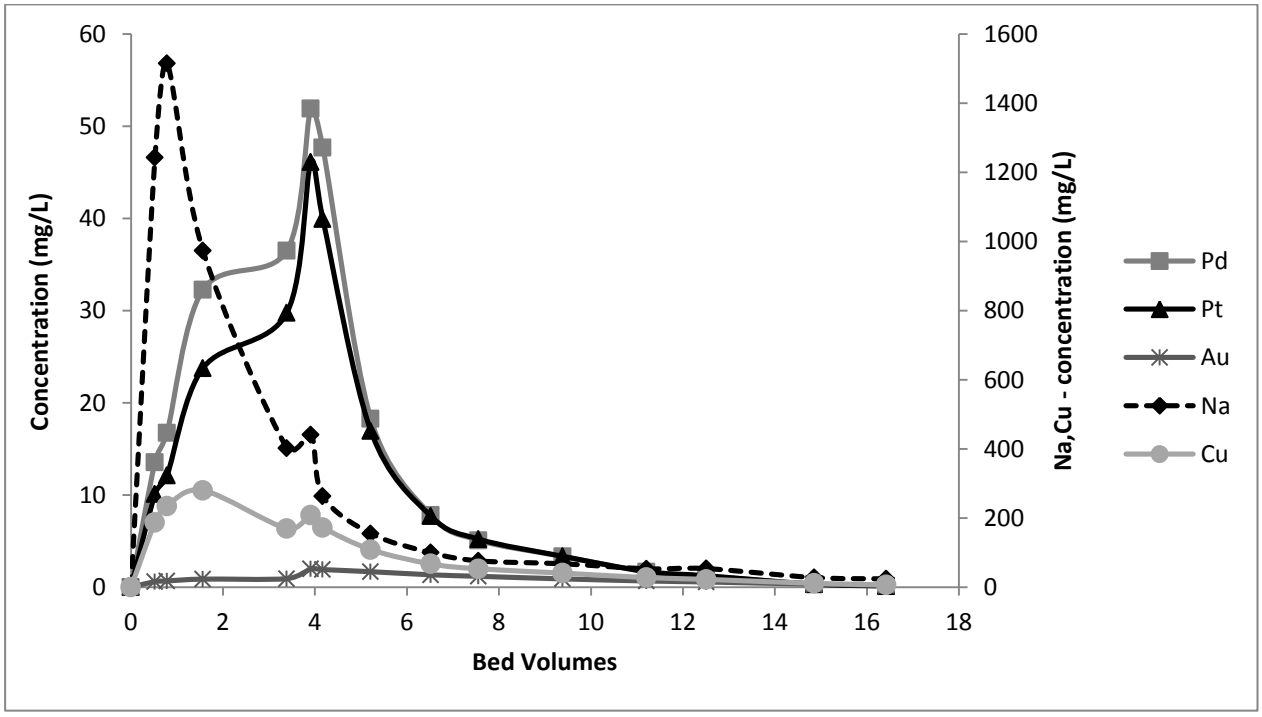
Elution experiment G

From carbon loading experiment A

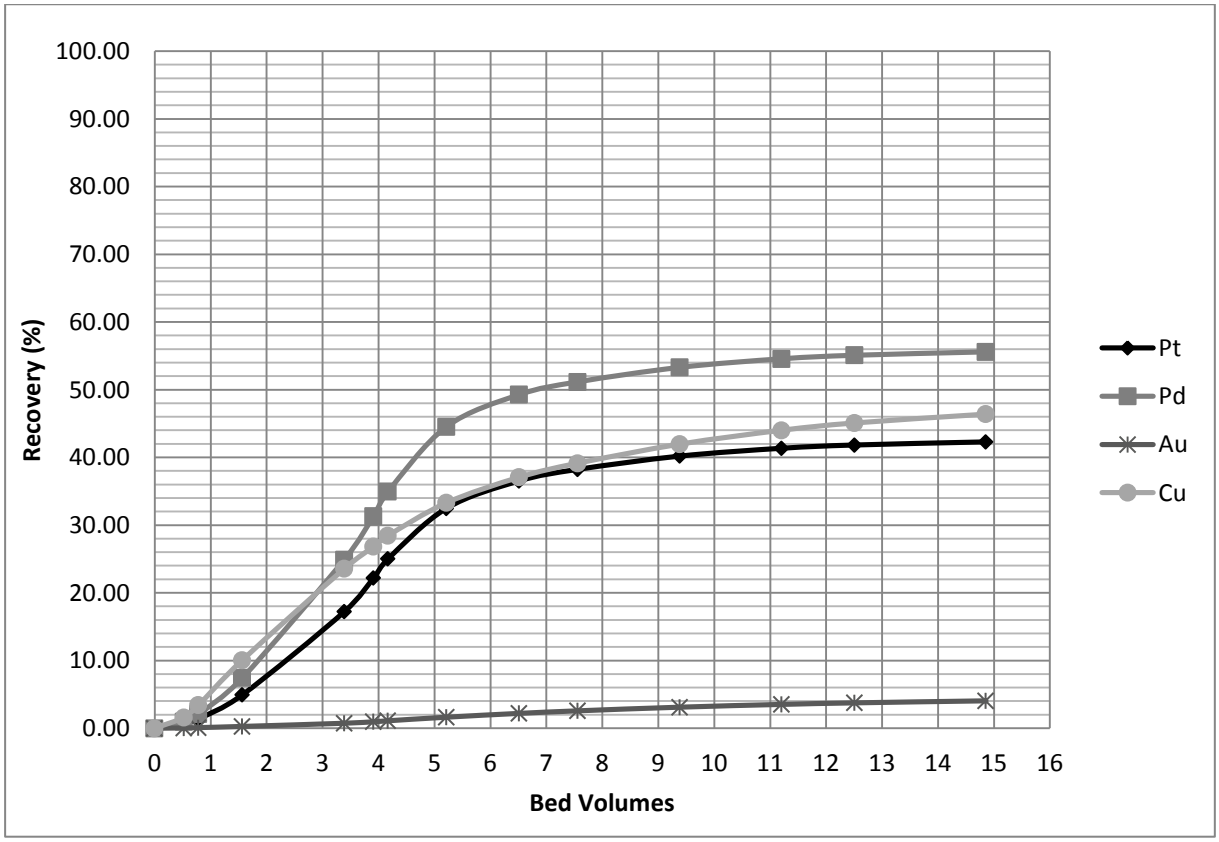
Date	08-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	13.18
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	9.84
Flow rate (BV/hr)	3.1

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NG1	0.02	49.45	2885	0.09	0.07					
water	NG2	< 0.001	3.20	6.1	< 0.001	< 0.001					
	NG3	0.60	187.30	1243.0	13.56	10.11	6.5	10:45	10:53	8	3.48
	NG4	0.68	234.50	1515.0	16.75	12.11	6.5	10:53	11:02	9	3.10
	NG5	0.88	279.90	973.3	32.25	23.76	5.5	11:02	11:15	13	1.81
	NG6	0.93	169.60	401.9	36.50	29.76	6.3	11:37	11:49	12	2.25
	NG7	1.99	208.70	441.2	51.91	46.12	6.6	11:50	11:58	8	3.54
	NG8	1.91	172.90	263.00	47.67	39.92	6.4	11:58	12:04	6	4.57
	NG9	1.68	108.40	155.10	18.26	16.96	7.5	12:19	12:27	8	4.02
	NG10	1.34	67.38	99.92	7.82	7.72	6.5	12:44	12:51	7	3.98
	NG11	1.18	52.97	76.10	5.09	5.20	6.5	13:00	13:09	9	3.10
	NG12	0.90	40.69	67.64	3.33	3.35	6.3	13:32	13:43	11	2.45
	NG13	0.67	27.60	53.23	1.67	1.70	5.6	14:12	14:22	10	2.40
	NG14	0.56	22.54	53.57	1.20	1.24	6	14:35	14:47	12	2.14
	NG15	0.32	11.07	27.76	0.33	0.33	7.8	15:19	15:28	9	3.71
	NG16	0.19	6.47	23.98	0.16	0.12	6.8	15:53	16:02	9	3.24



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)	Cu (mg)	Recovery (%)
0.00	0.00	0.05	0.00	0.04	0.00	0.00	0.00	0.68	0.00
7.30	0.52	0.06	0.99	0.04	0.66	0.00	0.04	0.77	1.61
10.95	0.78	0.27	2.09	0.20	1.39	0.01	0.09	2.82	3.42
21.90	1.56	0.88	7.43	0.68	4.92	0.02	0.27	5.74	10.05
47.44	3.39	0.32	24.91	0.28	17.22	0.01	0.74	1.38	23.57
54.74	3.91	0.18	31.34	0.16	22.20	0.01	0.95	0.70	26.82
58.39	4.17	0.48	34.96	0.42	25.02	0.03	1.10	2.05	28.46
72.98	5.21	0.24	44.54	0.23	32.48	0.03	1.63	1.60	33.30
91.23	6.52	0.09	49.28	0.09	36.53	0.02	2.19	0.88	37.07
105.83	7.56	0.11	51.15	0.11	38.23	0.03	2.57	1.20	39.14
131.37	9.38	0.06	53.29	0.06	40.19	0.02	3.11	0.87	41.96
156.91	11.21	0.03	54.56	0.03	41.35	0.01	3.52	0.46	44.01
175.16	12.51	0.03	55.09	0.03	41.83	0.01	3.75	0.55	45.09
208.00	14.86	0.01	55.59	0.00	42.29	0.01	4.04	0.19	46.39
229.90	16.42								
Sum		**2.80**		**2.36**		**0.20**		**19.89**	



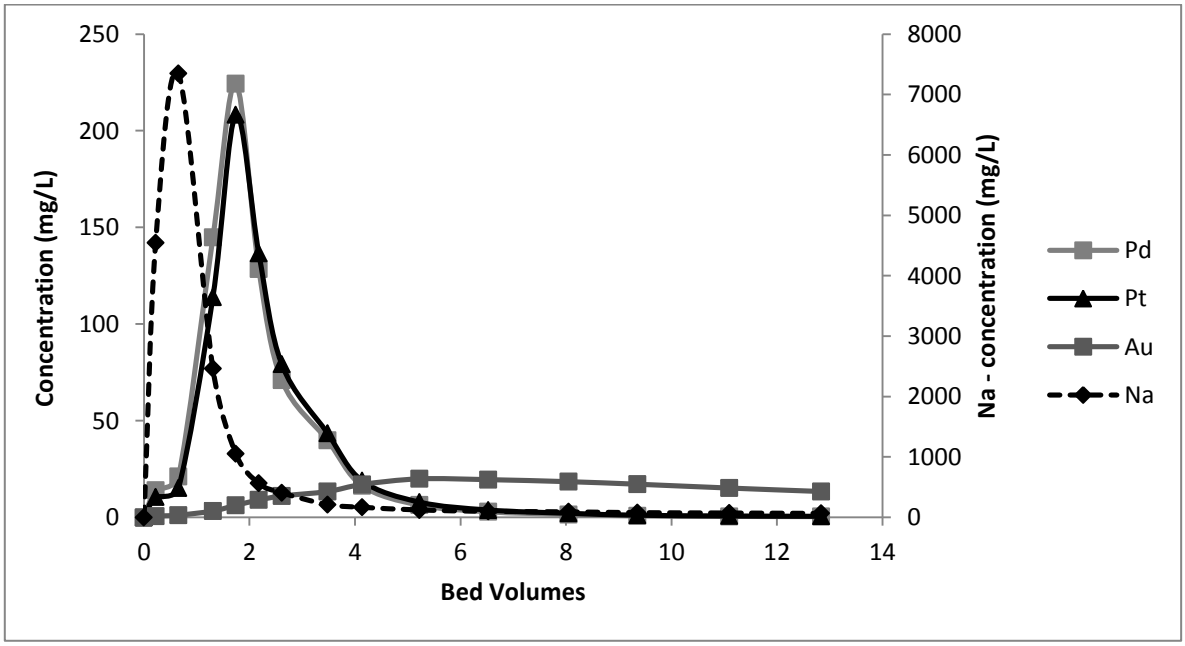
Elution experiment H

From carbon loading experiment 1 (30%) and A (70%)

Date	19-Jul
Pre-treatment step	
NaoH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.12
Activated Carbon (g)	16.87

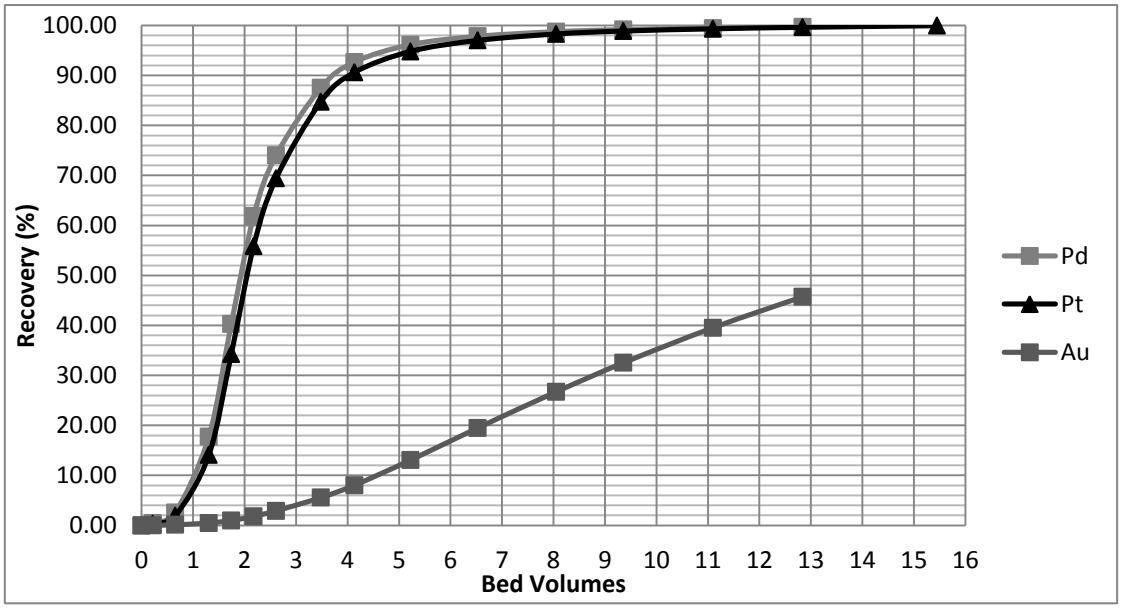
Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11.33
Flow rate (BV/hr)	2.6

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NH1	0.01	1.54	10570.0	0.04	0.04					
water	NH2	< 0.001	0.04	1.2	< 0.001	< 0.001					
	NH3	0.64	1.44	4544.0	14.06	10.47	7.4	10:59	11:02	3	10.57
	NH4	1.12	2.15	7348.0	21.14	15.17	6.1	11:02	11:15	13	2.01
	NH5	3.26	1.69	2462.0	144.80	113.90	6.1	11:15	11:27	12	2.18
	NH6	6.22	0.57	1050.0	224.40	208.20	6.3	11:27	11:40	13	2.08
	NH7	8.98	0.18	563.7	128.50	136.60	8.4	11:40	11:52	12	3.00
	NH8	11.03	0.11	405.9	70.91	79.17	5.8	11:52	12:01	9	2.76
	NH9	13.36	0.18	212.10	39.80	43.40	6.3	12:10	12:22	12	2.25
	NH10	17.01	0.18	166.20	16.40	18.92	6.9	12:26	12:34	12	2.46
	NH11	19.91	0.19	121.80	6.31	7.86	7.3	12:52	13:01	9	3.48
	NH12	19.49	0.19	99.71	2.86	3.79	7	13:22	13:32	10	3.00
	NH13	18.44	0.21	90.89	1.49	2.09	6.1	13:56	14:05	9	2.90
	NH14	17.13	0.22	77.32	0.78	1.08	6.4	14:25	14:34	9	3.05
	NH15	15.14	0.27	71.68	0.49	0.68	5.6	15:03	15:14	11	2.18
	NH16	13.37	0.49	64.94	0.38	0.53	7.2	15:42	15:55	13	2.37
	NH17	11.28	2.95	58.60	0.23	0.32	6.6	16:44	16:54	10	2.83
	NH18	16.39	0.03	112.40	5.38	6.20	7				



Mass Balance	Initial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	Weight AC in elution experiment (dry g)	Loading on sample (mg)
Batch 1 (40% of total)							
Pt	4.6	2	9.20	8	0.58	2.18	1.25
Pd	4.3	2	8.60	8	0.54	2.18	1.17
Au	6	2	12.00	8	0.75	2.18	1.64
Batch 2 (60% of total)							
Pt	5.541	2	11.08	8	0.69	5.09	3.52
Pd	5.7904	2	11.58	8	0.72	5.09	3.68
Au	6.242	2	12.48	8	0.78	5.09	3.97
Total							
Pt							4.78
Pd							4.86
Au					0.77		5.61

Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)	Na (mg)
0.00	0.00	0.02	**0.00**	0.02	0.00	0.00	0.00	7.00
3.08	0.22	0.11	0.43	0.08	0.33	0.01	0.02	36.03
9.14	0.65	0.76	2.57	0.59	1.93	0.02	0.11	44.83
18.28	1.31	1.12	17.77	0.98	14.07	0.03	0.47	10.70
24.37	1.74	1.08	40.30	1.05	34.25	0.05	0.99	4.92
30.46	2.18	0.61	61.85	0.66	55.87	0.06	1.81	2.95
36.56	2.61	0.67	74.02	0.75	69.39	0.15	2.90	3.77
48.74	3.48	0.26	87.54	0.28	84.76	0.14	5.55	1.73
57.88	4.13	0.17	92.69	0.20	90.62	0.28	8.03	2.19
73.11	5.22	0.08	96.15	0.11	94.81	0.36	13.05	2.02
91.39	6.53	0.05	97.83	0.06	97.00	0.40	19.48	2.03
112.71	8.05	0.02	98.76	0.03	98.29	0.33	26.71	1.54
130.99	9.36	0.02	99.17	0.02	98.89	0.39	32.51	1.82
155.36	11.10	0.01	99.48	0.01	99.33	0.35	39.53	1.66
179.73	12.84	0.01	99.69	0.02	99.63		45.74	2.26
216.29	15.45	0.01	99.91	0.01	99.95			
Sum		**4.99**		**4.87**		**2.56**		**125.44**



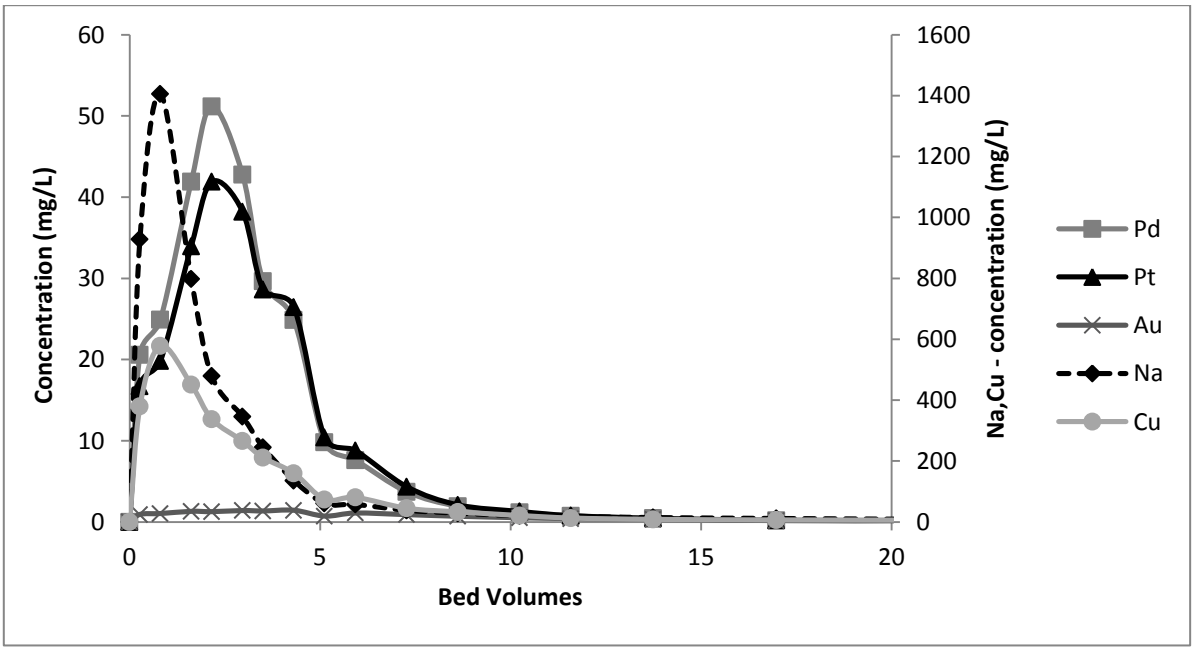
Elution experiment I

From carbon loading experiment B

Date	29-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	13.14
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	7.1
Flow rate (BV/hr)	3.2

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NI1	0.0358	37.02	3302	0.2909	0.1641					
water	NI2	0.0253	5.144	10.34	0.0373	0.1181					
	NI3	0.9264	379.1	927.8	20.58	16.71	6.2	09:44	09:52	8	3.32
	NI4	1.037	578.5	1406	24.93	19.82	6.4	09:52	10:03	11	2.49
	NI5	1.306	451.4	797.9	41.9	33.95	6.3	10:03	10:14	11	2.45
	NI6	1.265	337.9	479.1	51.18	41.89	6.2	10:14	10:26	12	2.21
	NI7	1.404	265.5	345.9	42.77	38.22	5.9	10:26	10:40	14	1.81
	NI8	1.352	211.1	245.3	29.63	28.62	6.7	10:40	10:48	8	3.59
	NI9	1.439	160.2	136.1	24.88	26.46	6.6	10:48	10:54	6	4.71
	NI10	0.72	73.99	60.90	9.80	10.42	5.6	11:09	11:19	10	2.40
	NI11	1.10	80.61	57.33	7.61	8.80	5.8	11:29	11:35	6	4.14
	NI12	0.90	44.79	38.20	3.71	4.33	6.4	11:54	12:01	7	3.92
	NI13	0.70	33.05	28.75	1.93	2.10	6.9	12:18	12:25	7	4.22
	NI14	0.52	21.11	20.31	1.17	1.29	6.2	12:47	12:54	7	3.80
	NI15	0.41	12.86	17.79	0.77	0.78	7.2	13:10	13:19	9	3.43
	NI16	0.31	8.43	14.38	0.46	0.44	6.8	13:50	13:59	9	3.24
	NI17	0.17	6.62	11.45	0.21	0.18	5.8	14:51	15:00	9	2.76
	NI18	0.16	5.99	8.28	0.17	0.20	6.6	16:17			
Bulk sample	NI19	0.55	31.70	26.85	2.69	3.00	8.2				



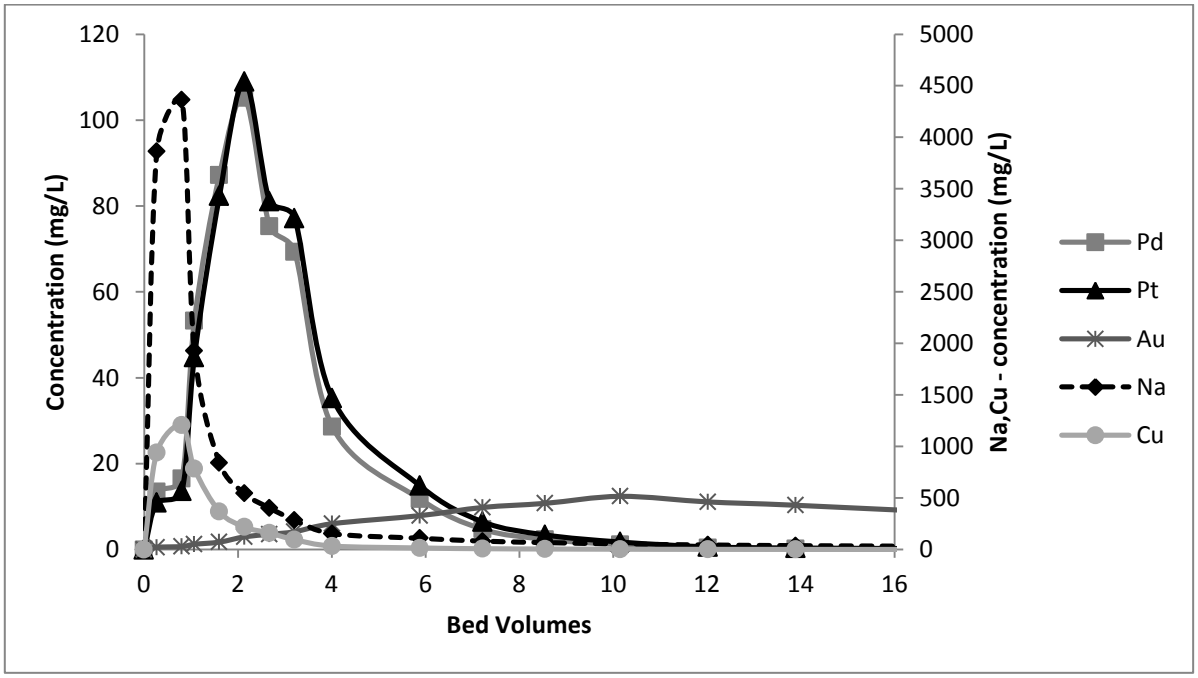
Elution experiment J

From carbon loading experiment B

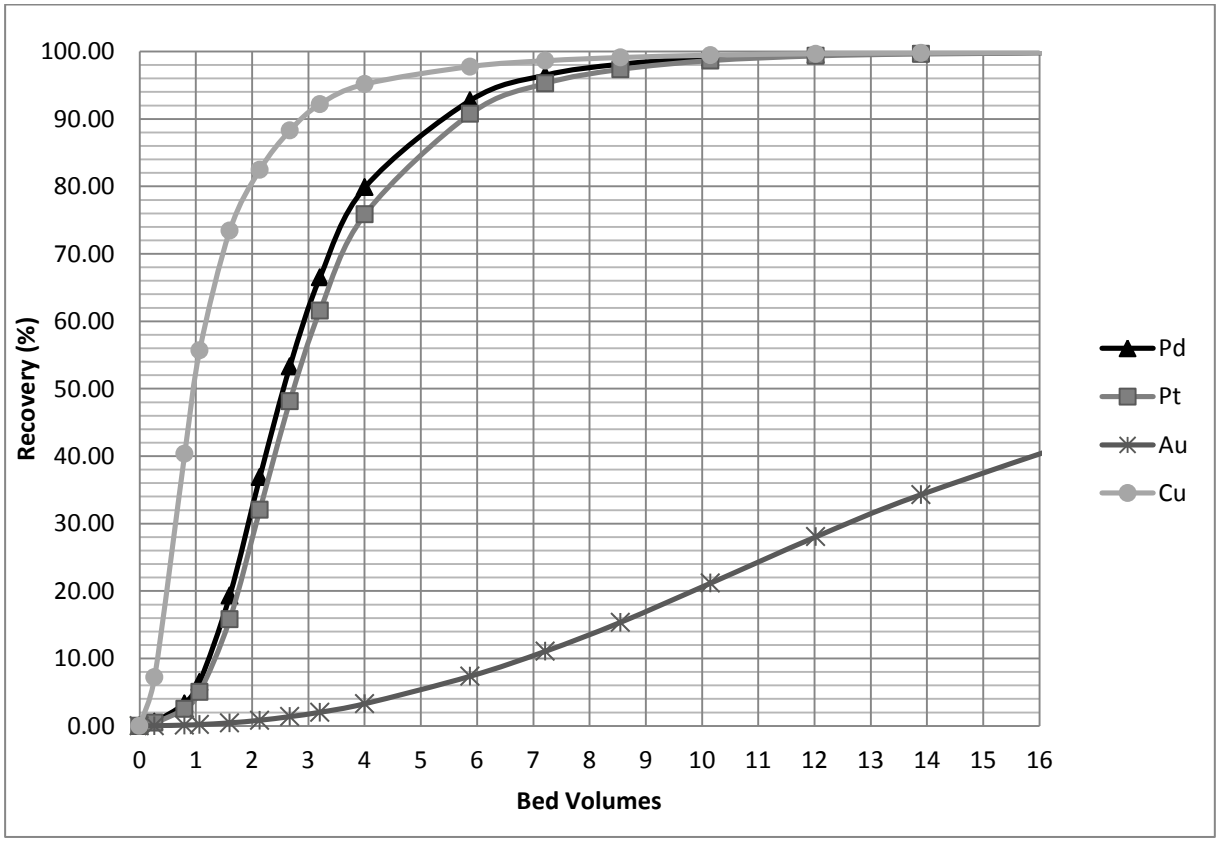
Date	29-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.38
Flow rate (BV/hr)	3.2

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NJ1	0.03	651.00	12430.00	0.18	0.08					
water	NJ2	0.03	1.17	3.27	nd	nd					
	NJ3	0.52	939.20	3863.00	13.48	10.94	6.7	10:39	10:46	7	4.10
	NJ4	0.69	1208.00	4362.00	16.54	13.61	6.3	10:46	10:53	7	3.86
	NJ5	1.21	784.20	1927.00	53.26	44.77	6.9	10:53	11:00	7	4.22
	NJ6	1.72	366.90	840.80	87.21	82.36	7	11:00	11:09	9	3.33
	NJ7	2.95	218.00	543.80	105.20	109.00	6.4	11:09	11:19	9.5	2.89
	NJ8	3.53	159.50	402.30	75.26	81.08	6.5	11:19	11:29	10.5	2.65
	NJ9	4.14	94.88	284.90	69.31	77.15	6.2	11:29	11:39	10	2.66
	NJ10	6.01	33.35	153.50	28.59	35.26	5.7	11:54	12:03	9	2.71
	NJ11	7.89	14.81	108.90	11.75	14.84	6.6	12:18	12:28	10	2.83
	NJ12	9.79	7.54	80.84	4.72	6.45	6.1	12:47	12:56	9	2.90
	NJ13	10.75	4.86	67.12	2.37	3.39	6.4	13:10	13:19	9	3.05
	NJ14	12.38	2.55	53.25	1.12	1.73	6.8	13:39	13:48	9	3.24
	NJ15	11.07	1.41	43.85	0.38	0.60	7	14:20	14:29	9	3.33
	NJ16	10.30	0.89	37.22	0.21	0.35	6.2	14:51	14:59	8	3.32
	NJ17	7.82	0.46	27.82	0.07	0.10	6.3	16:17	16:26	9	3.00
	NJ18	9.61	6.51	59.10	4.90	6.08	9.4				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)	Cu (mg)	Recovery (%)
0.00	0.00	0.03	0.00	0.02	0.00	0.00	0.00	1.76	0.00
3.74	0.27	0.11	0.61	0.09	0.46	0.00	0.02	8.03	4.14
11.22	0.80	0.13	3.35	0.11	2.55	0.00	0.12	3.73	23.05
14.97	1.07	0.53	6.53	0.48	5.02	0.01	0.20	4.31	31.83
22.45	1.60	0.72	19.33	0.72	15.81	0.02	0.45	2.19	41.97
29.93	2.14	0.68	36.87	0.71	32.04	0.02	0.84	1.41	47.13
37.41	2.67	0.54	53.32	0.59	48.16	0.03	1.38	0.95	50.45
44.90	3.21	0.55	66.49	0.63	61.58	0.06	2.02	0.72	52.69
56.12	4.01	0.53	79.88	0.66	75.88	0.18	3.30	0.63	54.39
82.31	5.88	0.15	92.75	0.20	90.76	0.17	7.37	0.21	55.87
101.02	7.22	0.07	96.50	0.09	95.27	0.19	11.07	0.12	56.36
119.72	8.55	0.04	98.11	0.06	97.35	0.26	15.36	0.08	56.64
142.17	10.15	0.02	99.07	0.03	98.66	0.31	21.17	0.05	56.83
168.36	12.03	0.01	99.55	0.01	99.35	0.28	28.04	0.03	56.95
194.55	13.90	0.01	99.74	0.01	99.63	0.61	34.30	0.05	57.03
261.89	18.71	0.00	99.97	0.00	99.97	0.11	47.95	0.01	57.13
289.06	20.65		100.00		100.00				100.00
Sum		**4.10**		**4.41**		**2.25**		**24.27**	



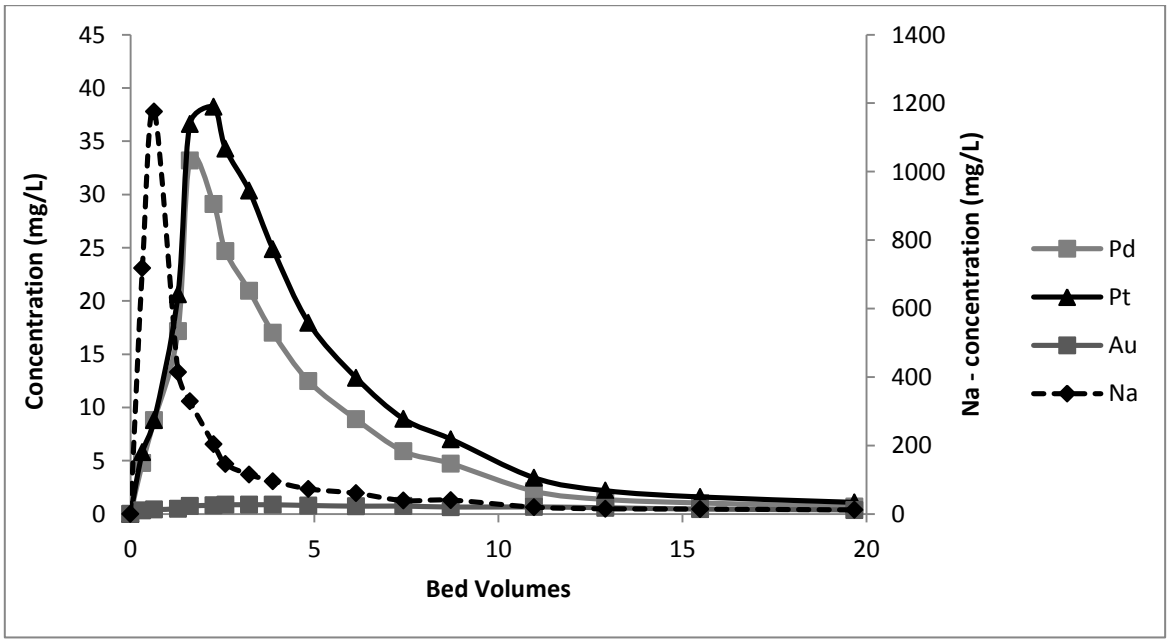
Elution experiment K

From loading experiment C

Date	08-Sep
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	13.5
Activated Carbon (wet g)	12

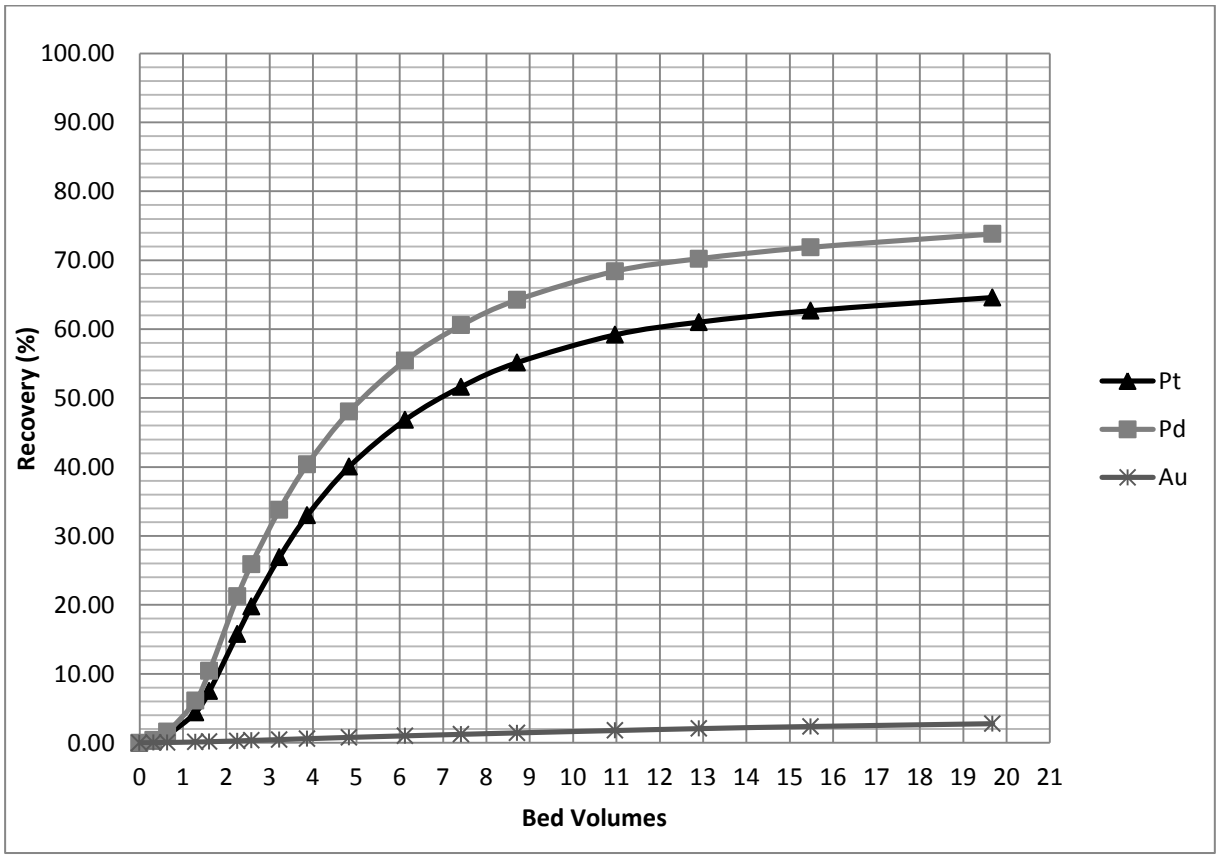
Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	10.4
Flow rate (BV/hr)	3.9

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NK1	0.11	0.02	2497.0	nd	nd					
water	NK2	nd	0.08	0.66	nd	nd					
	NK3	0.33	nd	718.50	4.77	5.81	6.4	10:13	10:18	5	5.91
	NK4	0.41	nd	1176.0	8.80	8.81	6.6	10:18	10:26	8	3.81
	NK5	0.48	nd	414.10	17.16	20.61	6.5	10:26	10:33	7	4.29
	NK6	0.75	nd	329.20	33.18	36.62	6.2	10:33	10:41	8	3.58
	NK7	0.80	nd	203.60	29.11	38.23	6.2	10:41	10:49	8	3.58
	NK8	0.86	nd	146.30	24.68	34.30	6.2	10:49	10:57	8	3.58
	NK9	0.86	nd	115.10	20.96	30.35	5.5	10:57	11:07	10	2.54
	NK10	0.86	nd	95.71	17.01	24.86	7	11:07	11:14	7	4.62
	NK11	0.80	nd	73.01	12.47	17.96	6.5	11:20	11:29	9	3.33
	NK12	0.73	nd	60.37	8.89	12.79	6.2	11:39	11:49	10	2.86
	NK13	0.74	nd	38.85	5.88	8.93	6.5	12:00	12:08	8	3.75
	NK14	0.65	nd	40.37	4.72	7.02	6	12:21	12:30	9	3.08
	NK15	0.66	nd	19.79	2.14	3.40	7.5	12:57	13:04	7.5	4.62
	NK16	0.58	nd	14.89	1.36	2.18	8.5	13:25	13:33	8	4.90
	NK17	0.46	nd	14.18	1.03	1.59	5.7	14:10	14:17	7	3.76
	NK18	0.38	nd	11.75	0.68	1.08	5.7	15:11	15:18	7	3.76
bulk	NK19	0.57	nd	45.20	2.98	4.44	7.5				



Mass Balance	Inintial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	dry AC (g)	PGM (mg)
Pt	5.31	4.00	21.25	8	0.664	5.73	3.80
Pd	3.38	4.00	13.52	8	0.423	5.73	2.42
Au	5.01	4.00	20.06	8	0.63	5.73	3.59

Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
4.19	0.32	0.03	0.41	0.03	0.32	0.00	0.01
8.39	0.65	0.11	1.59	0.12	1.13	0.00	0.04
16.78	1.29	0.11	6.09	0.12	4.37	0.00	0.11
20.97	1.61	0.26	10.45	0.31	7.52	0.01	0.15
29.36	2.26	0.11	21.24	0.15	15.77	0.00	0.27
33.55	2.58	0.19	25.90	0.27	19.77	0.01	0.33
41.94	3.23	0.16	33.80	0.23	26.90	0.01	0.46
50.33	3.87	0.19	40.38	0.27	32.98	0.01	0.59
62.91	4.84	0.18	48.04	0.26	40.07	0.01	0.77
79.69	6.13	0.12	55.45	0.18	46.84	0.01	1.00
96.46	7.42	0.09	60.56	0.13	51.63	0.01	1.22
113.24	8.71	0.10	64.24	0.15	55.15	0.02	1.43
142.60	10.97	0.04	68.40	0.07	59.17	0.02	1.77
167.76	12.90	0.04	70.22	0.06	61.01	0.02	2.05
201.32	15.49	0.05	71.87	0.07	62.68	0.02	2.36
255.84	19.68		73.80		64.59		
Sum		**1.79**		**2.46**		**0.15**	



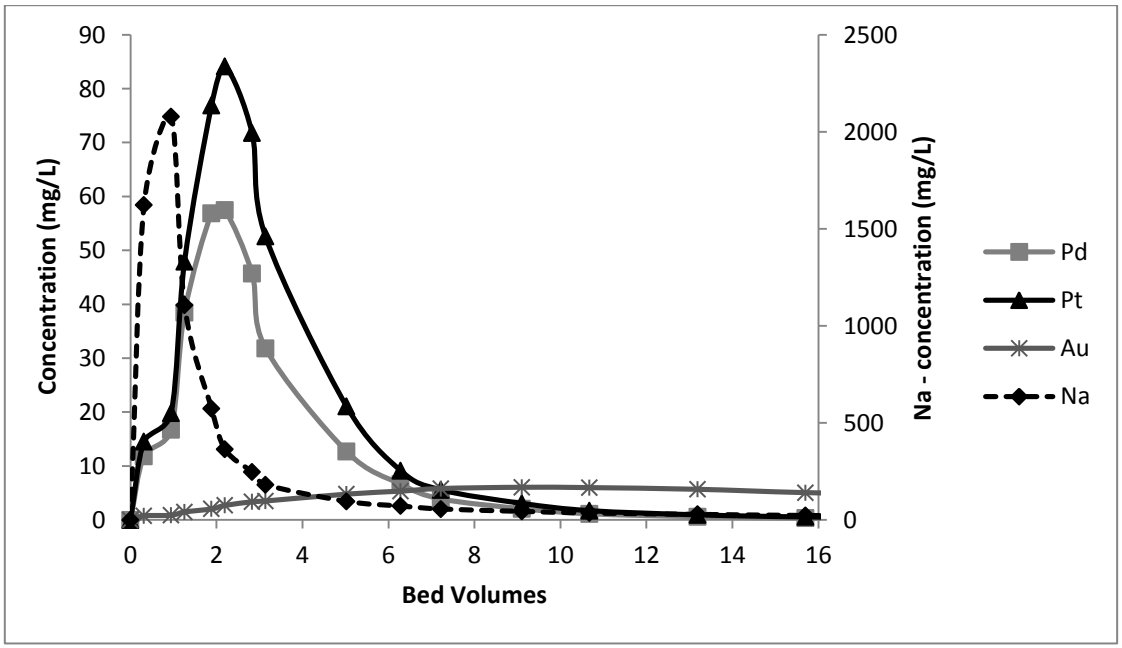
Elution experiment L

From loading experiment C

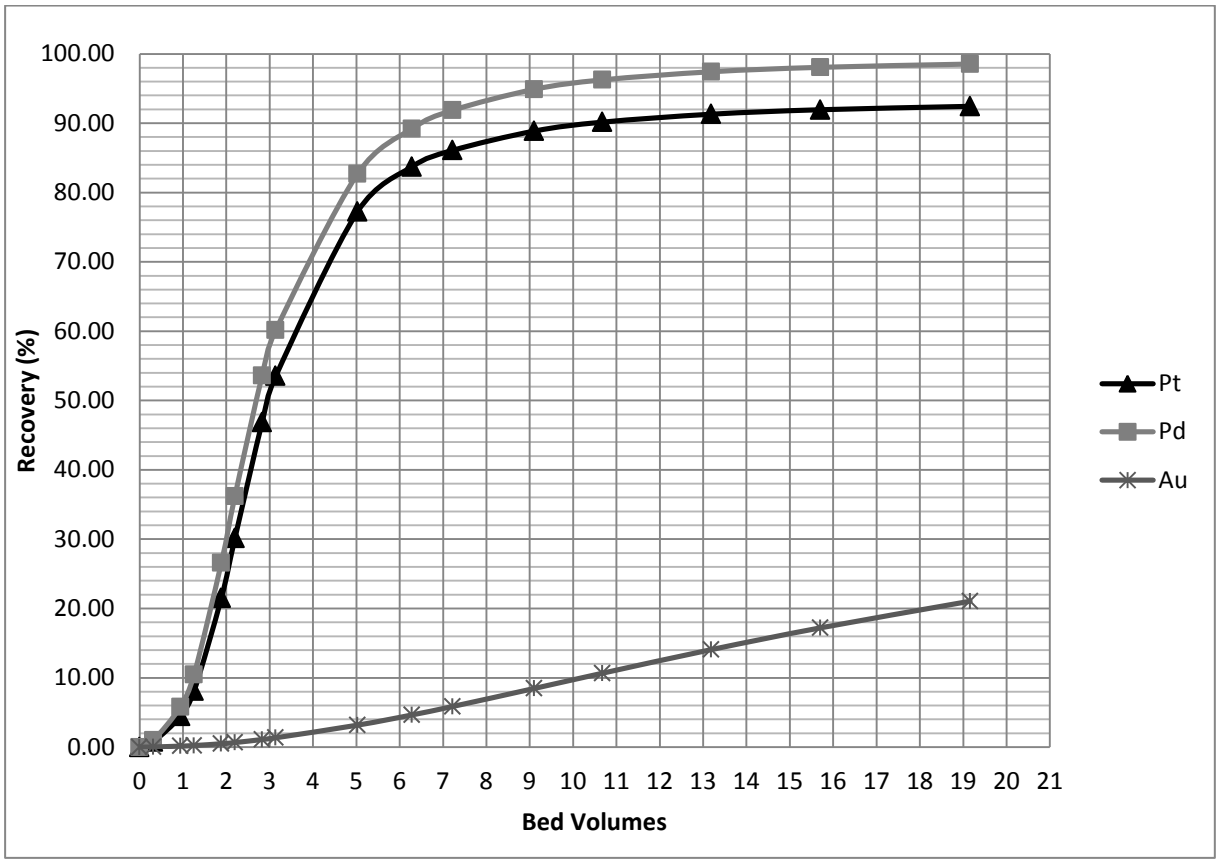
Date	08-Sep
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	1
Volume (mL)	40
Stirred (min)	30
pH	13.5
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	
Flow rate (BV/hr)	3.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NL1	nd	3.33	6067.0	nd	nd					
water	NL2	nd	0.06	0.53	nd	nd					
	NL3	0.75	2.97	1623.0	11.83	14.51	7	11:07	11:15	8	4.04
	NL4	0.88	3.17	2078.0	16.74	19.83	6.7	11:15	11:23	8	3.87
	NL5	1.47	1.68	1106.0	38.49	47.90	6.2	11:23	11:31	8	3.58
	NL6	2.04	0.80	574.40	56.89	76.89	6.5	11:31	11:39	8	3.75
	NL7	2.69	0.42	363.50	57.46	84.10	6.4	11:39	11:47	8	3.69
	NL8	3.37	0.23	246.70	45.73	71.77	6.5	11:47	11:55	8	3.75
	NL9	3.52	0.12	181.50	31.84	52.57	5.5	11:55	12:02	7	3.63
Water spillage	NL10	0.79	-0.05	23.79	4.24	8.25	6.5	12:02	12:10	8	3.75
	NL11	4.79	0.10	95.57	12.70	21.06	6.3	12:21	12:29	8	3.63
	NL12	5.34	0.06	71.66	6.65	9.16	7	12:40	12:49	9	3.59
	NL13	5.83	0.05	56.43	3.90	5.58	5.7	13:00	13:07	7	3.76
	NL14	6.06	0.04	44.09	2.08	3.07	6.6	13:25	13:33	8	3.81
	NL15	6.00	0.03	35.62	1.13	1.72	5.7	13:55	14:02	7	3.76
	NL16	5.68	0.02	28.67	0.61	0.95	5.8	14:32	14:39	7	3.82
	NL17	5.06	0.01	22.97	0.34	0.55	6.8	15:10	15:18	8	3.92
	NL18	4.52	0.01	17.92	0.17	0.28	6	16:06	16:13	7	3.96
	NL19	5.36	0.04	39.19	2.63	3.70	6.9				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.02	0.00	0.03	0.00	0.00	0.00
4.08	0.31	0.12	1.00	0.14	0.78	0.01	0.03
12.25	0.94	0.11	5.82	0.14	4.46	0.00	0.15
16.33	1.26	0.39	10.47	0.51	8.10	0.01	0.23
24.50	1.88	0.23	26.56	0.33	21.49	0.01	0.49
28.58	2.20	0.42	36.20	0.64	30.13	0.02	0.66
36.75	2.83	0.16	53.60	0.25	46.85	0.01	1.10
40.83	3.14	0.55	60.15	0.90	53.53	0.10	1.35
65.33	5.03	0.16	82.68	0.25	77.23	0.08	3.17
81.66	6.28	0.06	89.21	0.09	83.72	0.07	4.65
93.91	7.22	0.07	91.87	0.11	86.09	0.15	5.87
118.40	9.11	0.03	94.90	0.05	88.87	0.12	8.47
138.82	10.68	0.03	96.25	0.04	90.16	0.19	10.66
171.48	13.19	0.02	97.43	0.02	91.30	0.18	14.07
204.14	15.70	0.01	98.06	0.02	91.94	0.22	17.20
249.06	19.16		98.53		92.44		21.05
Sum		**2.39**		**3.52**		**1.18**	



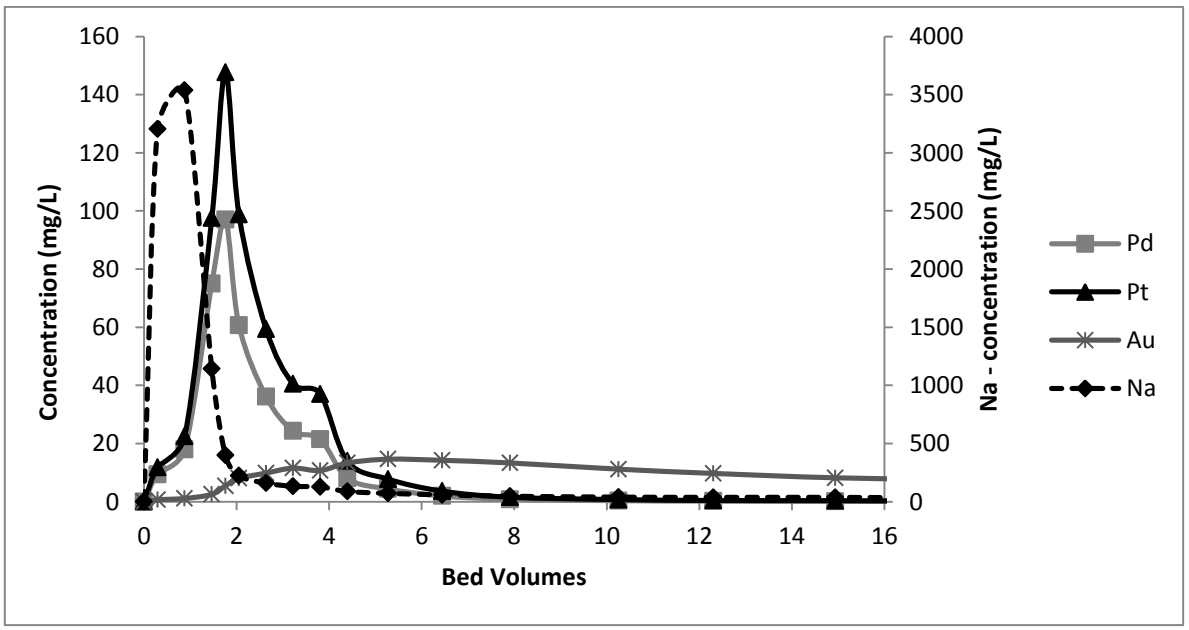
Elution experiment M

From loading experiment C

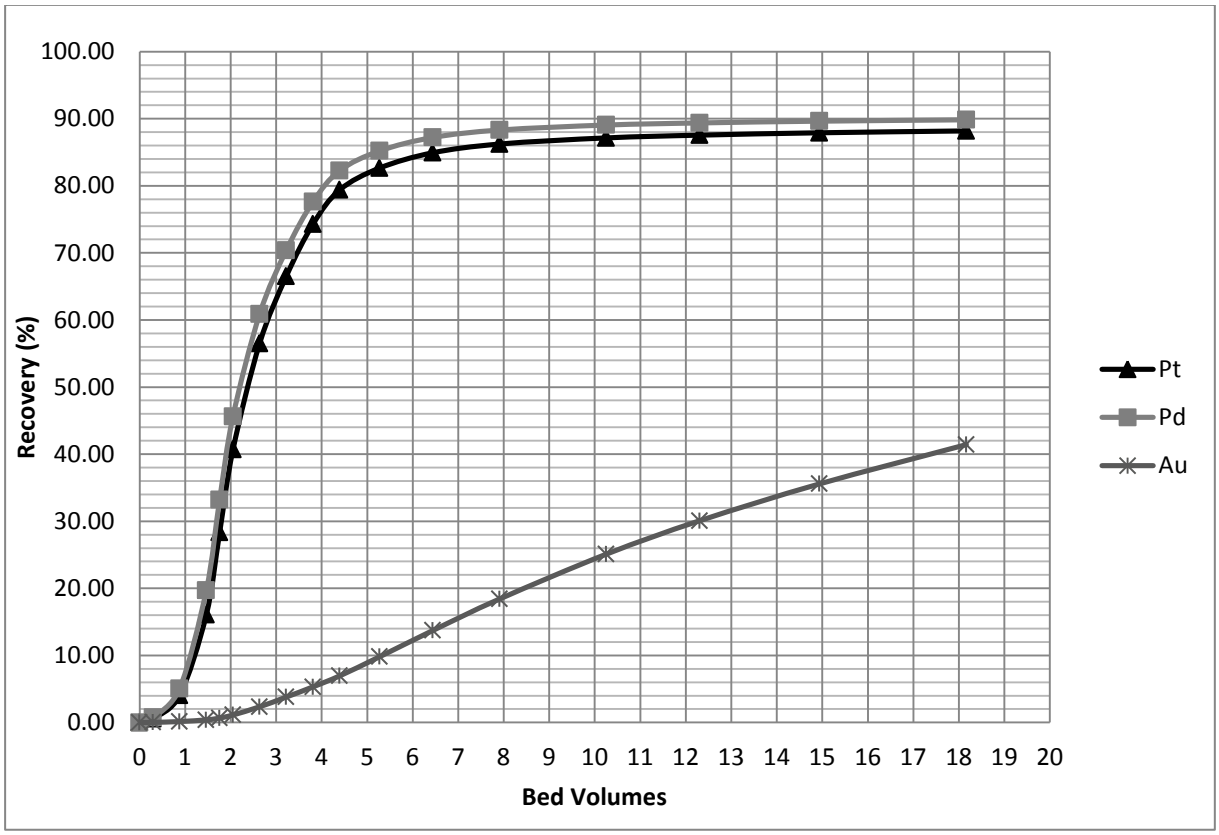
Date	09-Sep
Pre-treatment step	
NaOH (%)	0.275
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.3
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	
Flow rate (BV/hr)	3.5

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NM1	nd	1.18	8828.0	nd	nd					
water	NM2	nd	0.04	0.42	nd	nd					
	NM3	0.67	1.37	3204.0	9.44	11.82	6.4	09:37	09:46	9	3.28
	NM4	1.12	1.79	3539.0	18.03	22.54	6.5	09:46	09:58	12	2.50
	NM5	2.55	1.07	1142.0	74.96	97.62	6	09:58	10:04	6	4.62
	NM6	5.47	0.39	398.60	97.05	147.70	6.9	10:04	10:11	7	4.55
	NM7	8.02	0.16	224.00	60.72	98.83	5.8	10:11	10:17	6	4.46
	NM8	9.86	0.09	159.20	36.17	59.42	6.1	10:17	10:23	6	4.69
	NM9	11.56	0.06	132.80	24.38	40.54	5.9	10:23	10:32	9	3.03
	NM10	10.73	0.06	127.30	21.48	37.02	7	10:32	10:42	10	3.23
	NM11	13.33	0.06	88.37	8.08	13.96	5.6	10:48	10:55	7	3.69
	NM12	14.63	0.04	71.67	4.39	7.78	6.5	11:02	11:10	8	3.75
	NM13	14.24	0.03	59.25	1.99	3.63	7.2	11:21	11:31	10	3.32
	NM14	13.34	0.02	47.34	0.83	1.55	5.5	11:50	11:57	7	3.63
	NM15	11.20	0.02	39.85	0.36	0.74	5.9	12:27	12:36	9	3.03
	NM16	9.74	0.02	37.72	0.21	0.43	5.9	13:00	13:11	11	2.48
	NM17	8.23	0.02	37.71	0.17	0.36	5.9	13:47	13:57	10	2.72
	NM18	7.40	0.01	30.32	0.07	0.15	7.8	14:37	14:48	11	3.27
	NM19	10.57	0.04	43.69	1.32	2.40					



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00
3.81	0.29	0.10	0.74	0.13	0.59	0.01	0.02
11.42	0.88	0.35	5.06	0.46	4.03	0.01	0.14
19.04	1.46	0.33	19.69	0.47	16.06	0.02	0.39
22.85	1.76	0.30	33.22	0.47	28.34	0.03	0.67
26.66	2.05	0.37	45.63	0.60	40.67	0.07	1.13
34.27	2.64	0.23	60.87	0.38	56.51	0.08	2.34
41.89	3.22	0.17	70.40	0.30	66.52	0.08	3.80
49.51	3.81	0.11	77.61	0.19	74.28	0.09	5.31
57.12	4.39	0.07	82.26	0.12	79.39	0.16	6.95
68.55	5.27	0.05	85.20	0.09	82.65	0.22	9.80
83.78	6.44	0.03	87.21	0.05	84.93	0.26	13.73
102.82	7.91	0.02	88.31	0.03	86.23	0.37	18.42
133.29	10.25	0.01	89.06	0.02	87.14	0.28	25.09
159.95	12.30	0.01	89.37	0.01	87.55	0.31	30.08
194.22	14.94	0.00	89.64	0.01	87.90	0.33	35.57
236.12	18.16	0.00	89.84	0.00	88.19	0.09	41.42
Sum		**2.17**		**3.36**		**2.32**	



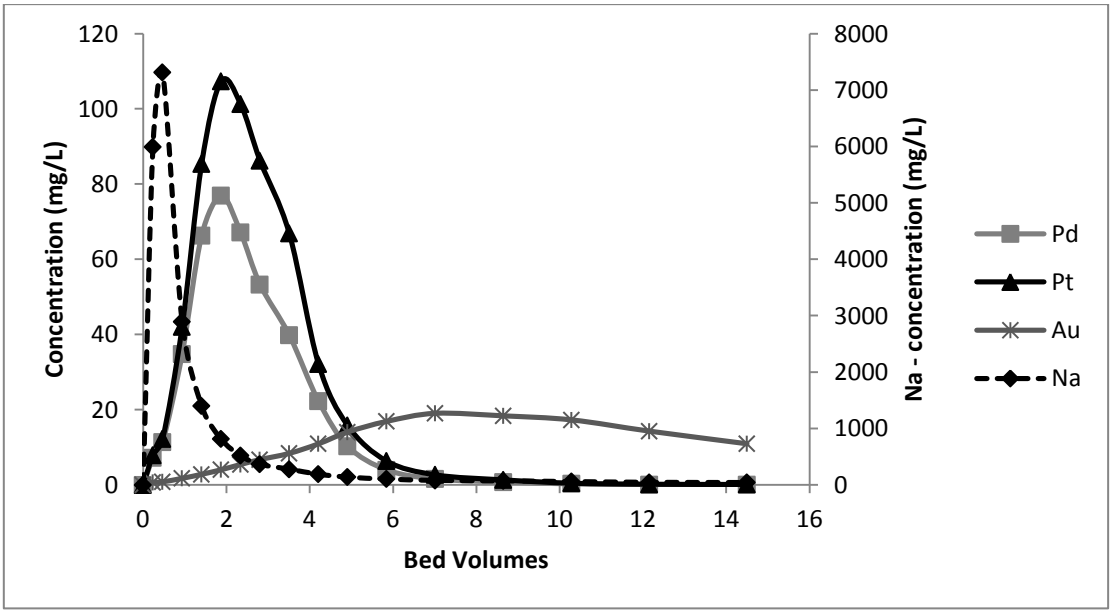
Elution experiment N

From loading experiment C

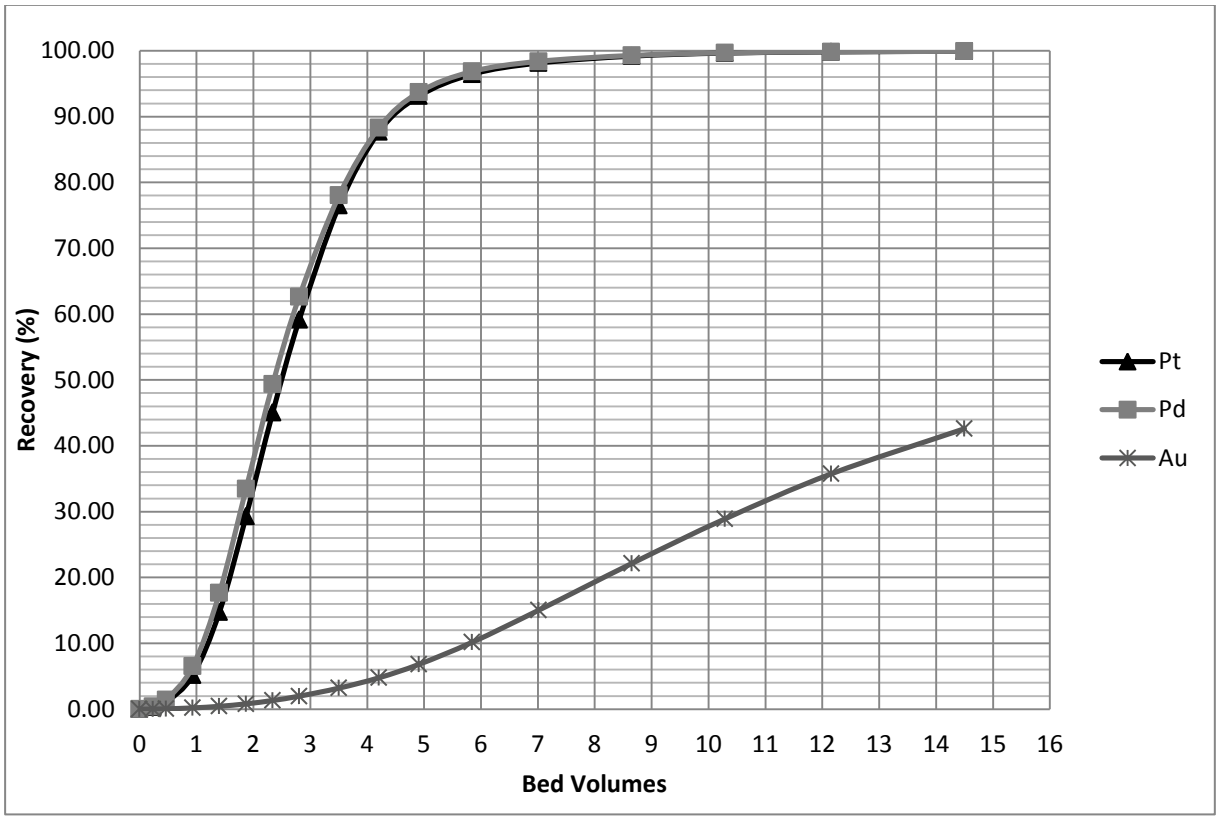
Date	09-Sep
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	4
Volume (mL)	40
Stirred (min)	30
pH	13.5
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	13.6
Flow rate (BV/hr)	2.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	NN1	nd	0.62	20580.0	nd	nd					
water	NN2	nd	0.06	0.51	nd	0.01					
	NN3	0.61	0.92	5993.0	7.16	7.90	5.8	10:37	10:43	6	4.46
	NN4	0.79	1.00	7311.0	11.38	12.21	5.6	10:43	10:51	8	3.23
	NN5	1.73	0.79	2891.0	34.79	42.01	6	10:51	11:01	10	2.77
	NN6	2.80	0.55	1401.0	66.25	85.31	6.5	11:01	11:11	10	3.00
	NN7	4.01	0.33	813.90	76.95	107.30	5.8	11:11	11:20	9	2.97
	NN8	5.42	0.20	516.80	67.15	101.30	6.4	11:20	11:31	11	2.69
	NN9	6.72	0.14	366.00	53.27	86.21	5.6	11:31	11:42	11	2.35
	NN10	8.37	0.10	278.20	39.84	66.89	5.4	11:42	11:53	11	2.27
	NN11	10.91	0.10	188.60	22.29	32.18	5.6	11:59	12:10	11	2.35
	NN12	14.04	0.08	137.10	10.30	15.78	5.9	12:16	12:26	10	2.72
	NN13	16.87	0.06	102.80	3.99	6.33	5.6	12:37	12:46	9	2.87
	NN14	19.02	0.05	78.53	1.58	2.65	6.8	13:00	13:11	11	2.85
	NN15	18.35	0.04	70.99	0.75	1.31	5.5	13:32	13:44	12	2.12
	NN16	17.27	0.02	58.34	0.27	0.44	5.9	14:10	14:21	11	2.48
	NN17	14.28	0.02	45.30	0.09	0.16	6	14:50	14:58	8	3.46
	NN18	10.93	0.02	41.42	0.06	0.10	5.5	15:37	15:48	11	2.31
	NN19	14.00	0.05	69.70	2.27	3.34					



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
3.04	0.23	0.03	0.39	0.03	0.30	0.00	0.02
6.08	0.47	0.14	1.42	0.16	1.06	0.01	0.05
12.16	0.94	0.31	6.51	0.39	5.15	0.01	0.19
18.24	1.40	0.44	17.66	0.59	14.75	0.02	0.44
24.32	1.87	0.44	33.45	0.63	29.28	0.03	0.81
30.40	2.34	0.37	49.34	0.57	45.01	0.04	1.32
36.48	2.81	0.42	62.63	0.70	59.16	0.07	1.98
45.60	3.51	0.28	78.03	0.45	76.48	0.09	3.21
54.72	4.21	0.15	88.31	0.22	87.69	0.11	4.78
63.83	4.91	0.09	93.70	0.13	93.11	0.19	6.81
75.99	5.85	0.04	96.86	0.07	96.45	0.27	10.16
91.19	7.01	0.02	98.39	0.04	98.14	0.40	15.03
112.47	8.65	0.01	99.29	0.02	99.19	0.38	22.13
133.75	10.29	0.00	99.68	0.01	99.65	0.38	28.90
158.07	12.16	0.00	99.84	0.00	99.83	0.38	35.75
188.46	14.50	0.00	99.92	0.00	99.93	0.81	42.59
		2.76		**4.03**		**2.39**	



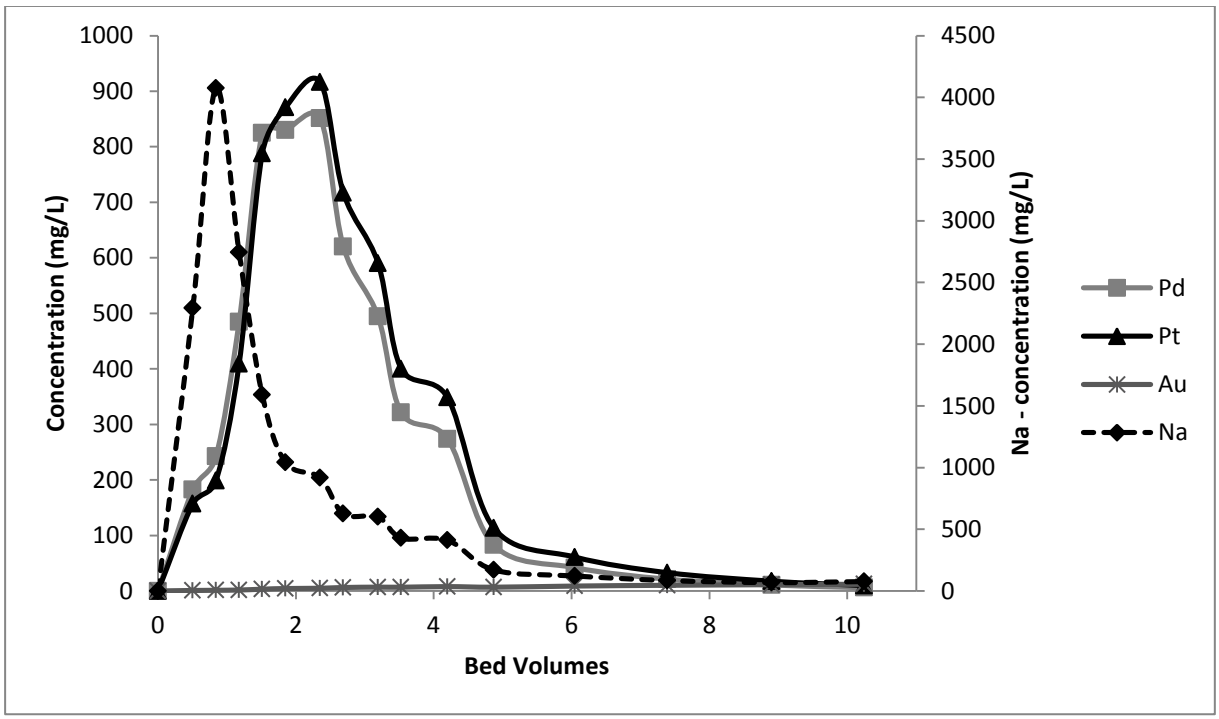
Elution experiment High

From loading experiment High

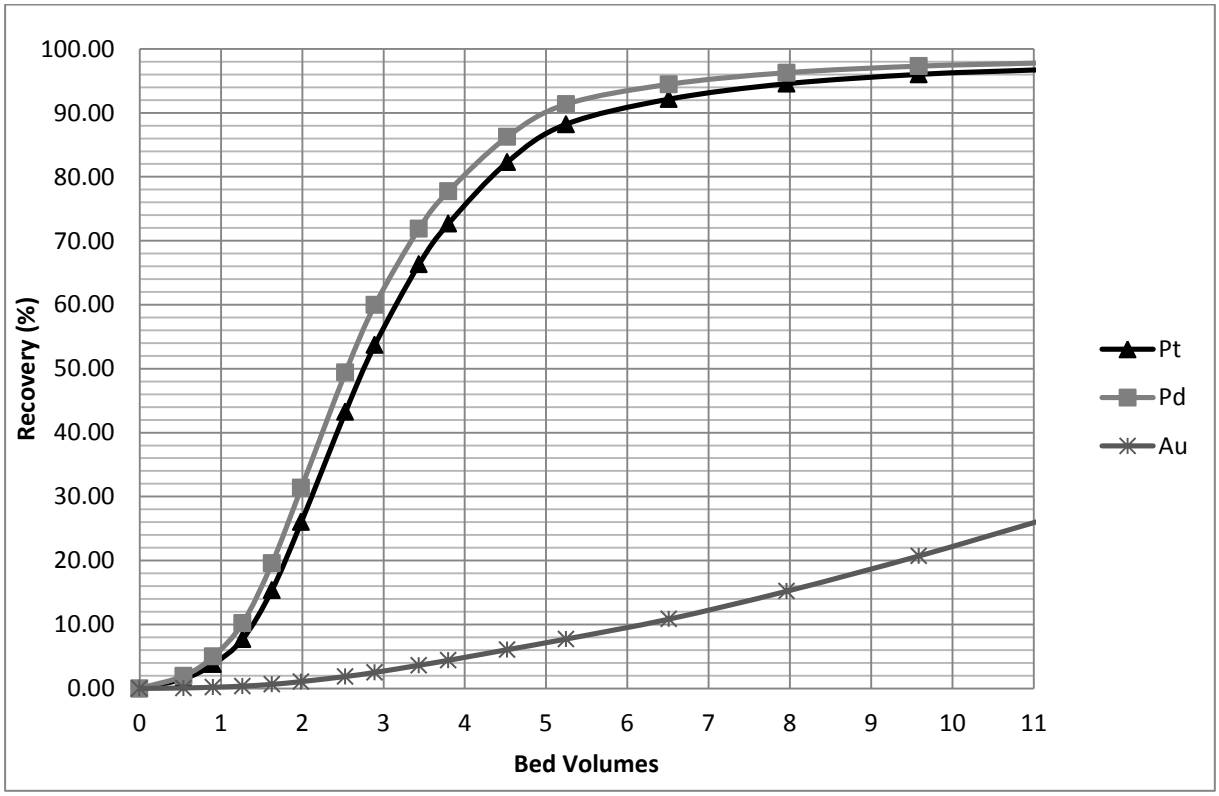
Date	03-Apr
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
Flow rate (BV/hr)	2.0

	mg/L	Au	Na	Pd	Pt	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	AK1	0.20	17000.0	0.95	0.69					
water	AK2	nd	3.39	0.01	0.02					
	AK3	0.87	2293.0	182.50	157.00	5.1	10:32	10:46	14	1.56
	AK4	1.21	4075.0	242.30	198.60	5.4	10:46	10:56	10	2.31
	AK5	1.70	2743.0	484.60	409.00	5.4	10:56	11:05	11	2.10
	AK6	3.21	1589.0	824.70	788.00	5.4	11:05	11:15	10	2.31
	AK7	4.41	1043.00	829.90	870.60	5.4	11:15	11:25	10	2.31
	AK8	4.89	917.40	851.40	916.50	5	11:25	11:41	16	1.34
	AK9	6.27	625.70	620.20	717.20	5.5	11:41	11:51	10	2.36
	AK10	6.88	599.40	494.30	590.30	5.9	11:51	12:03	12	2.11
	AK11	6.72	428.70	321.30	400.10	5.1	12:03	12:15	12	1.82
	AK12	7.83	411.80	273.80	348.40	5.3	12:21	12:34	13	1.75
	AK13	6.77	170.10	82.59	113.50	5.3	12:44	12:54	10	2.27
	AK14	8.88	121.40	42.00	61.06	5.6	13:20	13:31	11	2.18
	AK15	10.24	84.33	21.21	32.87	5	13:58	14:09	11	1.95
	AK16	11.30	67.79	10.79	17.60	7.5	14:40	14:55	15	2.14
	AK17	12.13	76.11	5.86	9.66	5.2	15:23	15:36	13	1.71



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.64	0.00	0.55	0.00	0.00	0.00
7.60	0.54	1.00	1.96	0.84	1.51	0.00	0.07
12.66	0.90	1.71	5.00	1.43	3.80	0.01	0.19
17.73	1.27	3.08	10.19	2.82	7.70	0.01	0.36
22.80	1.63	3.89	19.56	3.90	15.38	0.02	0.64
27.86	1.99	5.93	31.39	6.30	26.03	0.03	1.07
35.46	2.53	3.46	49.43	3.84	43.24	0.03	1.87
40.52	2.89	3.93	59.95	4.61	53.73	0.05	2.50
48.12	3.44	1.92	71.91	2.33	66.32	0.03	3.63
53.19	3.80	2.80	77.74	3.52	72.68	0.07	4.40
63.32	4.52	1.68	86.25	2.17	82.29	0.07	6.06
73.45	5.25	1.03	91.35	1.44	88.22	0.13	7.72
91.18	6.51	0.59	94.47	0.88	92.15	0.18	10.84
111.44	7.96	0.34	96.28	0.53	94.56	0.23	15.20
134.24	9.59	0.16	97.31	0.26	96.02	0.22	20.72
	11.04	0.73	97.78	1.20	96.72	1.51	26.06
	28.01		100.00		100.00		
Sum		**32.89**		**36.63**		**2.58**	



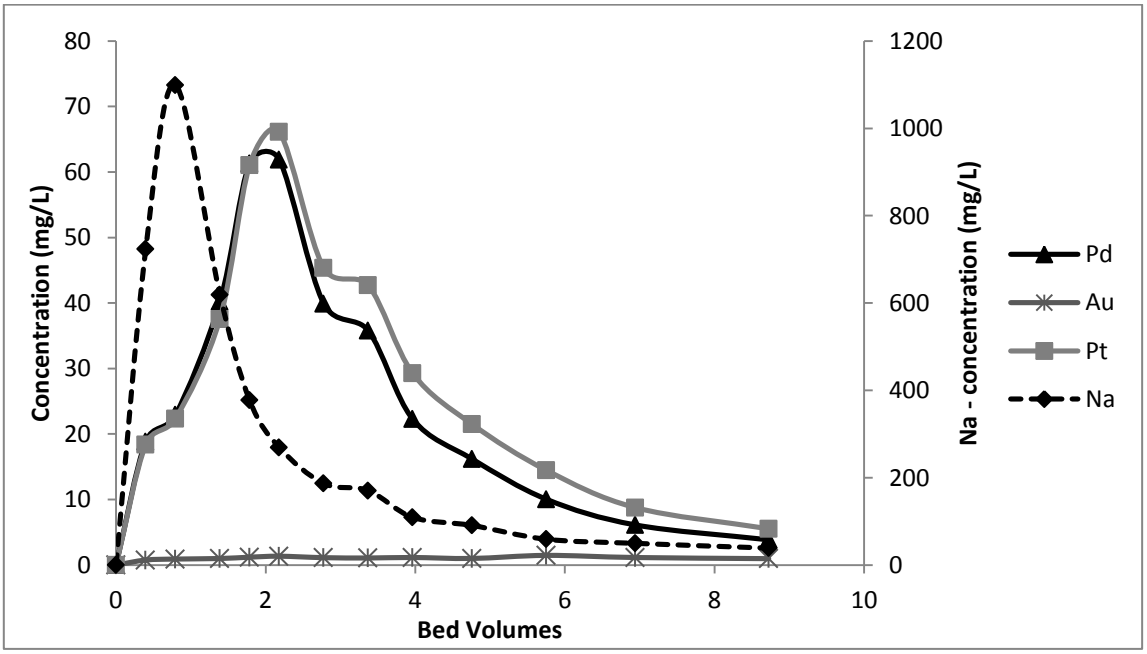
Elution experiment O

Loading experiment D

Date	07-Jul
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	12.94
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.22
Flow rate (BV/hr)	2.4

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	O1	nd	nd	3158.00	nd	nd					
water	O2	nd	0.01	0.43	nd	nd					
	O3	0.76	0.05	723.50	18.83	18.40	6	09:57	10:06	9	2.86
	O4	0.91	0.02	1099.00	22.92	22.34	5.6	10:06	10:17	11	2.18
	O5	0.99	0.01	619.20	40.17	37.56	5.1	10:17	10:30	13	1.68
	O6	1.20	nd	377.70	61.32	61.04	6.1	10:30	10:41	11	2.38
	O7	1.35	nd	269.40	61.89	66.15	5.3	10:41	10:52	11	2.06
	O8	1.12	0.02	186.70	39.91	45.37	8	10:52			
	O9	1.07	nd	170.50	35.79	42.70	6.4	11:06	11:19	13	2.11
	O10	1.15	nd	109.20	22.27	29.26	5.9	11:25	11:35	10	2.53
	O11	1.00	nd	90.65	16.19	21.50	6	11:40	11:53	13	1.98
	O12	1.47	0.00	59.13	10.05	14.48	5.8	12:15	12:22	7	3.55
	O13	1.15	0.00	49.63	6.12	8.77	5.4	12:42	12:52	10	2.31
	O14	0.97	0.00	38.72	3.85	5.54	5.9	13:22	13:33	10	2.53
bulk	O15	1.07	0.00	50.27	7.44	10.09	8.6				



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.05	0.00	0.05	0.00	0.00	0.00
5.55	0.40	0.12	1.24	0.11	1.00	0.00	0.04
11.10	0.79	0.26	3.99	0.25	3.22	0.01	0.13
19.43	1.39	0.28	10.23	0.27	8.11	0.01	0.28
24.98	1.78	0.34	16.93	0.35	13.48	0.01	0.40
30.53	2.18	0.42	25.05	0.46	20.40	0.01	0.54
38.86	2.78	0.32	35.12	0.37	29.50	0.01	0.73
47.19	3.37	0.24	42.60	0.30	36.69	0.01	0.91
55.52	3.97	0.21	48.35	0.28	42.57	0.01	1.09
66.62	4.76	0.18	53.42	0.25	48.09	0.02	1.32
80.50	5.75	0.13	57.74	0.19	52.99	0.02	1.65
97.15	6.94	0.12	60.94	0.18	56.79	0.03	2.07
122.14	8.72		63.90		60.29		2.58
Sum		**2.69**		**3.07**		**0.13**	

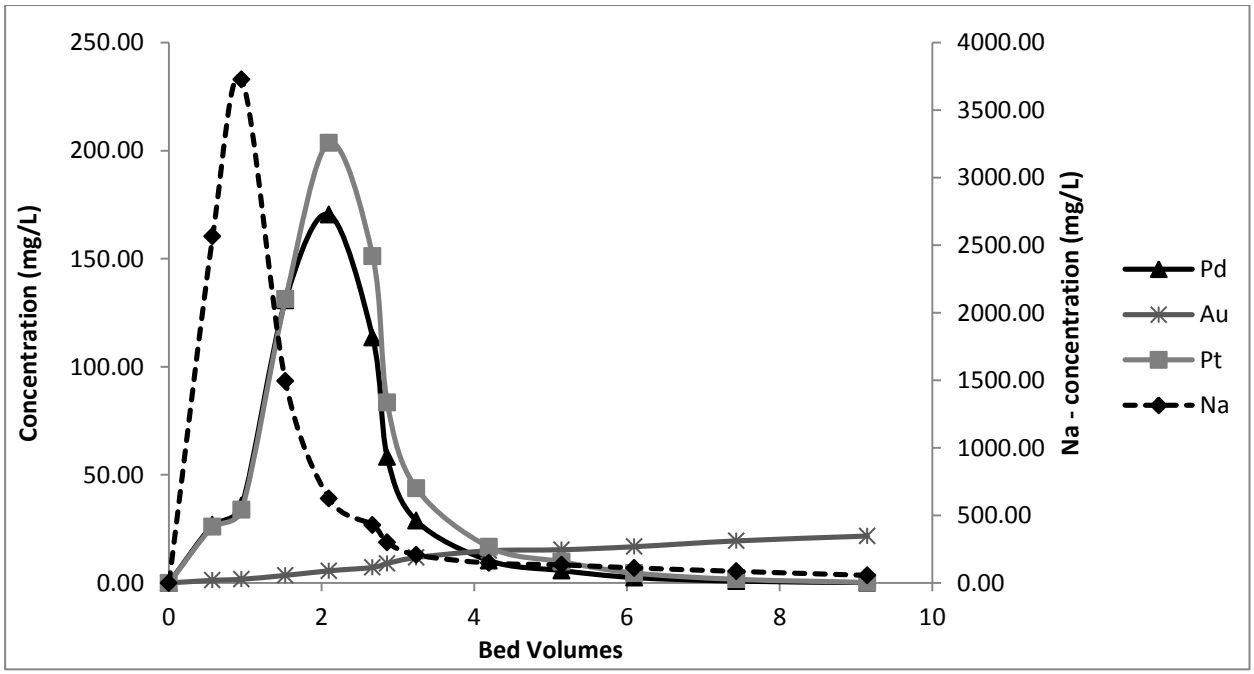
Elution experiment P

Loading experiment D

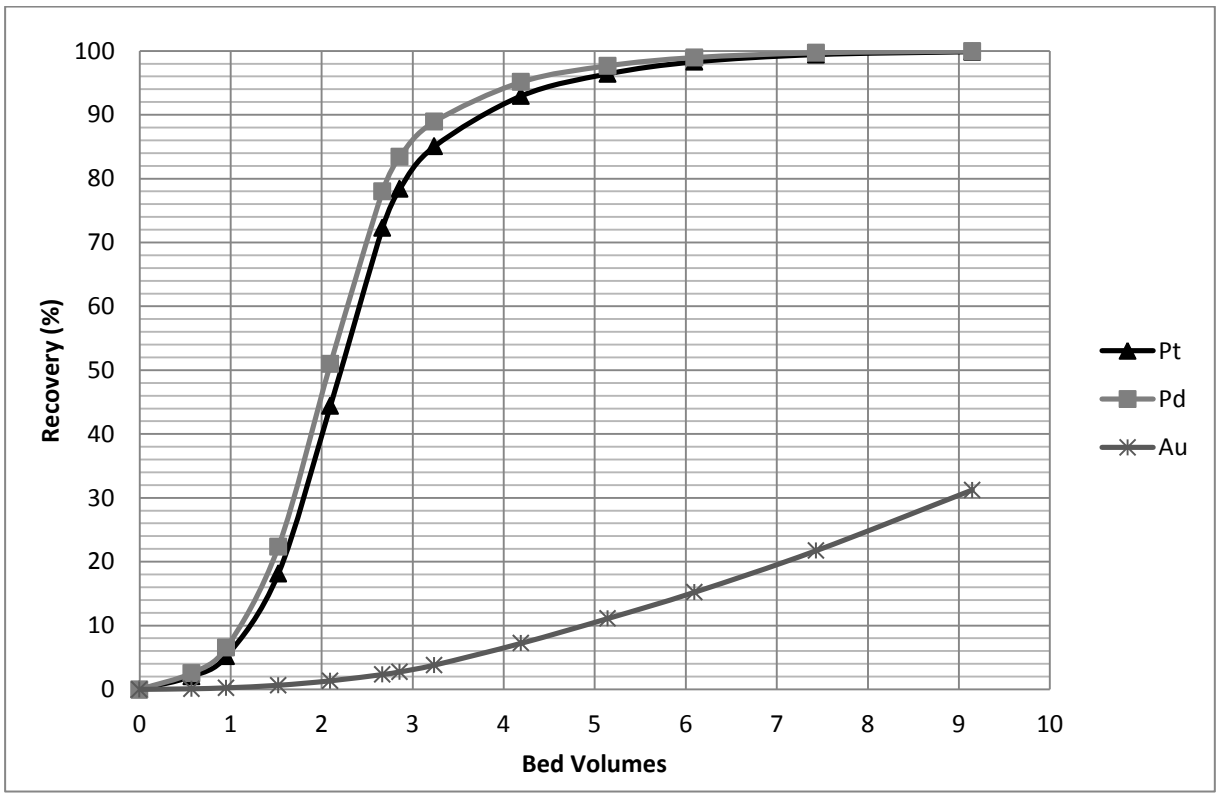
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	12.84
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.62
Flow rate (BV/hr)	2.3

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	P1	nd	0.67	11640.00	nd	nd					
water	P2	nd	0.01	0.54	nd	nd					
	P3	1.21	2.28	2565.00	26.85	26.03	5.5	11:06	11:19	13	1.81
	P4	1.70	1.93	3726.00	35.78	33.84	5.3	11:19	11:32	13	1.75
	P5	3.48	1.21	1494.00	130.70	131.30	5.8	11:32	11:45	13	1.91
	P6	5.62	0.40	625.30	170.50	203.60	5.5	11:45	12:00	15	1.57
	P7	7.17	0.15	429.00	113.50	151.20	5	12:00	12:13	13	1.65
	P8	9.02	0.07	299.80	58.23	83.44	5.7	12:13	12:21	8	3.05
	P9	11.75	0.04	206.60	28.76	43.80	5.5	12:21	12:31	10	2.36
	P10	14.87	0.03	147.10	10.34	16.62	5.3	12:42	12:54	12	1.89
	P11	15.37	0.02	133.50	5.70	9.80	5.6	13:10	13:20	10	2.40
	P12	16.77	0.02	111.30	2.46	4.56	6.8	13:35	13:45	10	2.91
	P13	19.45	0.01	85.63	0.85	1.68	7.2	14:06	14:20	14	2.20
	P14	21.70	0.01	56.08	0.11	0.23	5.5	14:59	15:05	6	3.93
bulk	P15	18.32	0.03	99.47	4.08	6.63	8.2				



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.11	0.00	0.10	0.00	0.00	0.00
8.00	0.57	0.17	2.55	0.16	2.04	0.01	0.09
13.34	0.95	0.67	6.52	0.66	5.17	0.02	0.24
21.34	1.52	1.21	22.35	1.34	18.13	0.04	0.64
29.35	2.10	1.14	50.98	1.42	44.41	0.05	1.34
37.35	2.67	0.23	77.98	0.31	72.26	0.02	2.33
40.02	2.86	0.23	83.42	0.34	78.39	0.06	2.74
45.36	3.24	0.26	88.93	0.40	85.05	0.18	3.81
58.70	4.19	0.11	95.13	0.18	92.95	0.20	7.22
72.04	5.15	0.05	97.67	0.10	96.41	0.21	11.10
85.38	6.10	0.03	98.96	0.06	98.29	0.34	15.22
104.05	7.43	0.01	99.70	0.02	99.43	0.49	21.73
128.07	9.15	0.00	99.97	0.00	99.88		31.23
Sum		**4.21**		**5.09**		**1.62**	



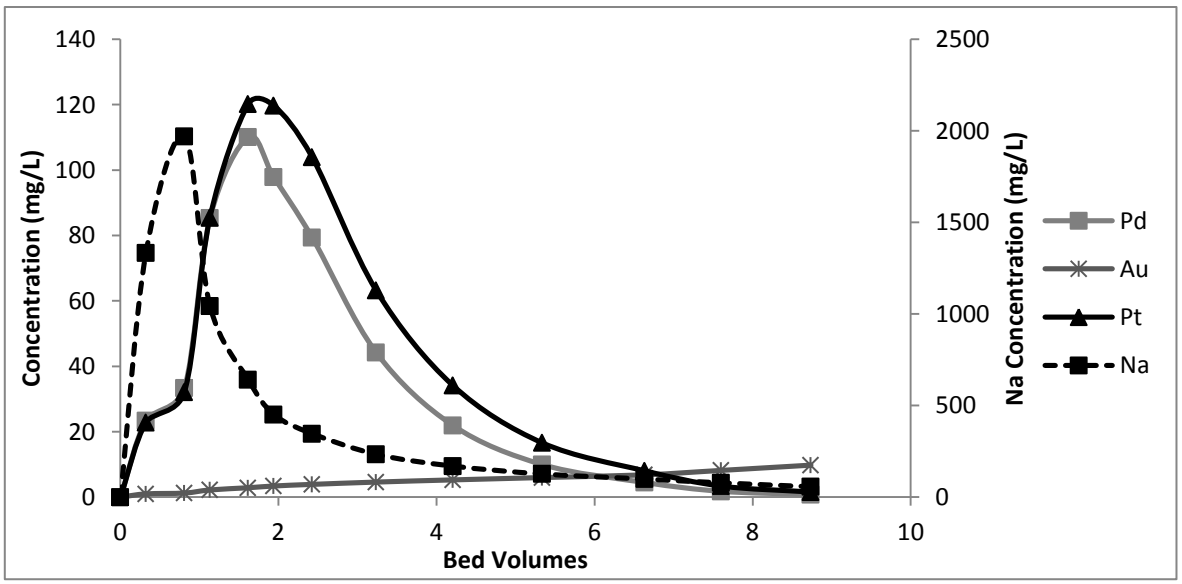
Elution experiment Q

Loading experiment D

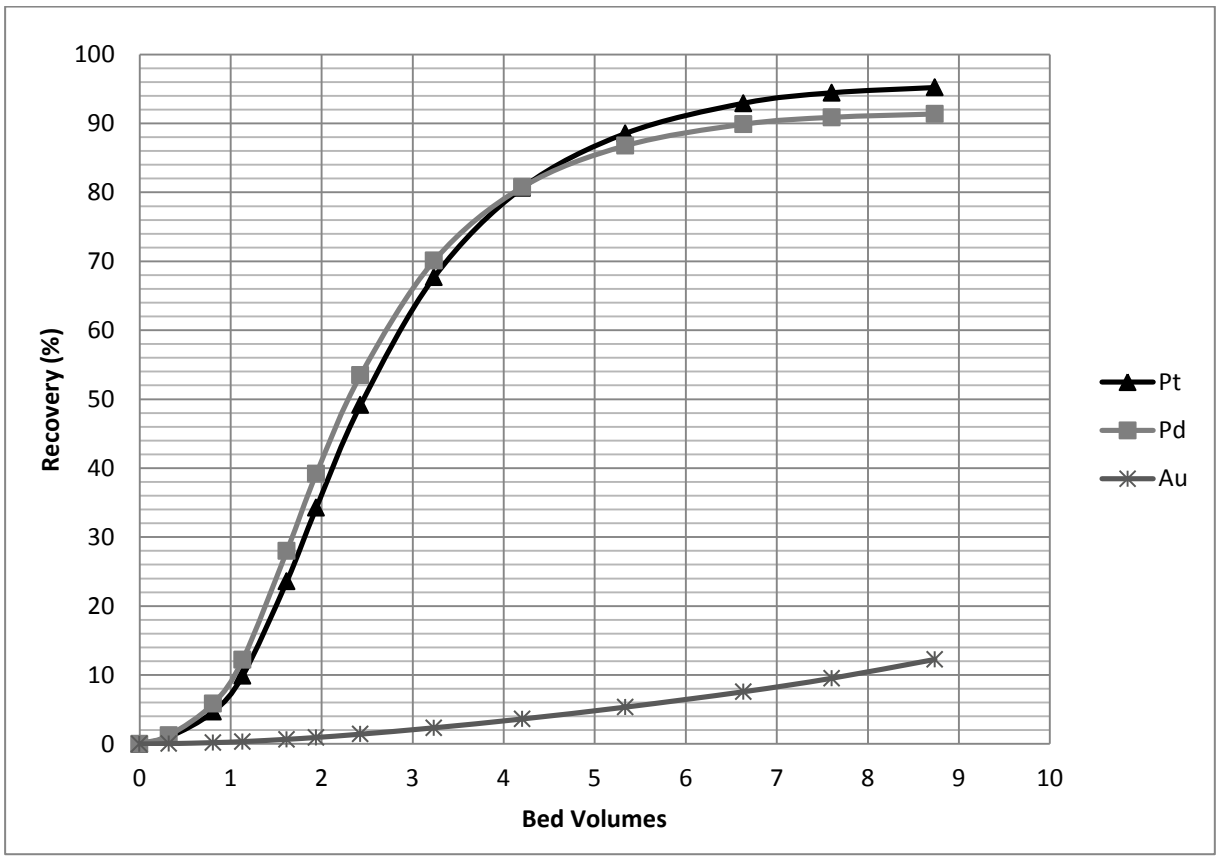
Date	25-Nov
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	1
Volume (mL)	40
Stirred (min)	30
pH	12.77
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.5
Flow rate (BV/hr)	1.9

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	Q1	nd	0.43	7237.00	nd	nd					
water	Q2	nd	0.01	0.58	nd	nd					
	Q3	0.98	1.41	1334.00	23.39	22.79	5.6	09:55	10:06	11	2.18
	Q4	1.24	1.79	1970.00	33.37	32.13	5.8	10:06	10:19	13	1.91
	Q5	2.19	1.04	1044.00	85.32	85.47	5.5	10:19	10:31	12	1.96
	Q6	2.86	0.49	640.30	110.10	120.20	5.6	10:31	10:44	13	1.85
	Q7	3.40	0.28	451.20	97.82	119.70	5.5	10:44	10:57	13	1.81
	Q8	3.89	0.19	346.50	79.35	103.90	5	10:57	11:10	13	1.65
	Q9	4.59	0.09	233.50	44.22	63.20	5.7	11:22	11:37	15	1.63
	Q10	5.26	0.05	169.20	21.92	34.14	5.8	11:51	12:07	16	1.55
	Q11	5.98	0.03	126.30	9.94	16.57	5.4	12:26	12:41	15	1.54
	Q12	6.81	0.02	98.40	4.48	8.04	5.5	13:04	13:19	15	1.57
	Q13	8.17	0.01	77.71	1.76	3.36	6.4	13:42	13:52	10	2.74
	Q14	9.77	0.01	56.59	0.78	1.56	5.4	14:15	14:23	8	2.89
bulk	Q15	7.61	0.04	107.20	10.63	16.07					



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.05	0.00	0.05	0.00	0.00	0.00
4.53	0.32	0.19	1.26	0.19	1.01	0.01	0.04
11.33	0.81	0.27	5.84	0.27	4.67	0.01	0.19
15.86	1.13	0.66	12.23	0.70	9.89	0.02	0.34
22.65	1.62	0.47	28.00	0.54	23.60	0.01	0.67
27.18	1.94	0.60	39.18	0.76	34.25	0.02	0.94
33.98	2.43	0.70	53.48	0.95	49.15	0.05	1.41
45.30	3.24	0.45	70.10	0.66	67.70	0.07	2.34
58.89	4.21	0.25	80.78	0.40	80.67	0.09	3.63
74.75	5.34	0.13	86.78	0.22	88.55	0.12	5.34
92.87	6.63	0.04	89.88	0.08	92.92	0.10	7.57
106.46	7.60	0.02	90.89	0.04	94.44	0.14	9.52
122.31	8.74		91.37		95.21		12.26
Sum		**3.85**		**4.86**		**0.64**	



Elution experiment R

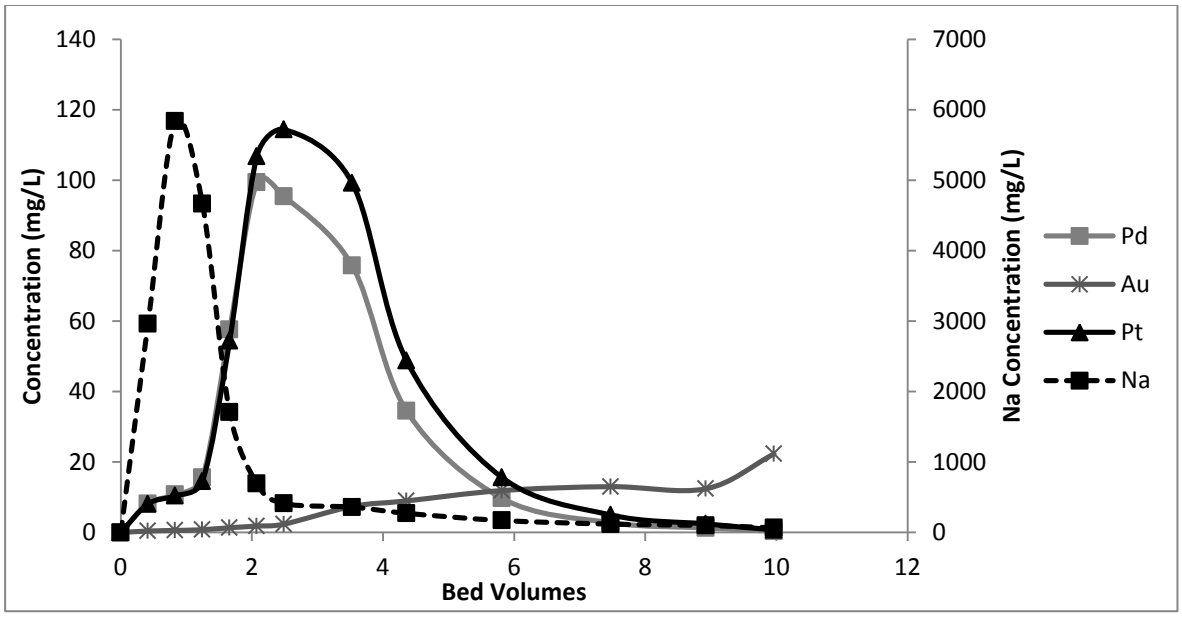
Loading experiment D

Date	25-Nov
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	3
Volume (mL)	40
Stirred (min)	30
pH	12.72
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80*
Bed Volume (mL)	14
pH after	10.77
Flow rate (BV/hr)	2.3

*Temperature loss occurring during elution run due to non flow through the column jacket.

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	R:1	nd	0.86	15020.00	nd	nd					
water	R:2	nd	0.02	0.68	nd	nd					
	R:3	0.41	0.71	2961.00	8.19	8.10	5.4	10:53	11:07	14	1.65
	R:4	0.58	1.41	5839.00	10.77	10.44	5.9	11:07	11:16	9	2.81
	R:5	0.79	1.16	4665.00	15.59	14.57	6.2	11:16	11:27	11	2.42
	R:6	1.35	0.75	1706.00	57.57	54.40	6	11:27	11:37	10	2.57
	R:7	1.82	0.45	693.80	99.42	106.80	5.4	11:37	11:45	8	2.89
	R:8	2.37	0.28	411.60	95.46	114.40	5.4	11:45	11:53	8	2.89
	R:9	7.38	0.18	360.50	75.78	99.25	5.3	12:08	12:20	12	1.89
	R:10	8.96	0.08	272.10	34.52	48.82	5.4	12:30	12:42	12	1.93
	R:11	11.90	0.03	170.20	9.73	15.65	5.6	13:03	13:16	13	1.85
	R:12	13.01	0.02	118.80	2.78	4.98	5.3	13:42	13:58	16	1.42
	R:13	12.41	0.01	99.20	1.29	2.43	7	14:16	14:29	13	2.31
	R:14	22.30	0.01	65.85	0.35	0.75	5.1	14:47	14:54	7	3.12
bulk	R:15	13.26	0.08	166.30	21.43	29.26					



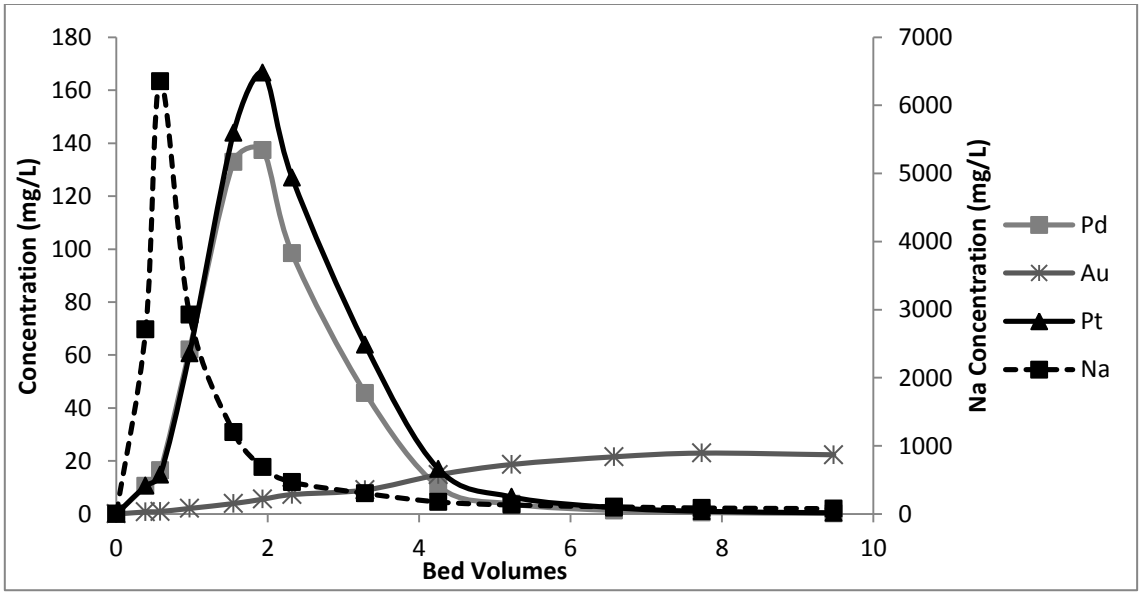
Elution experiment S

Loading experiment D

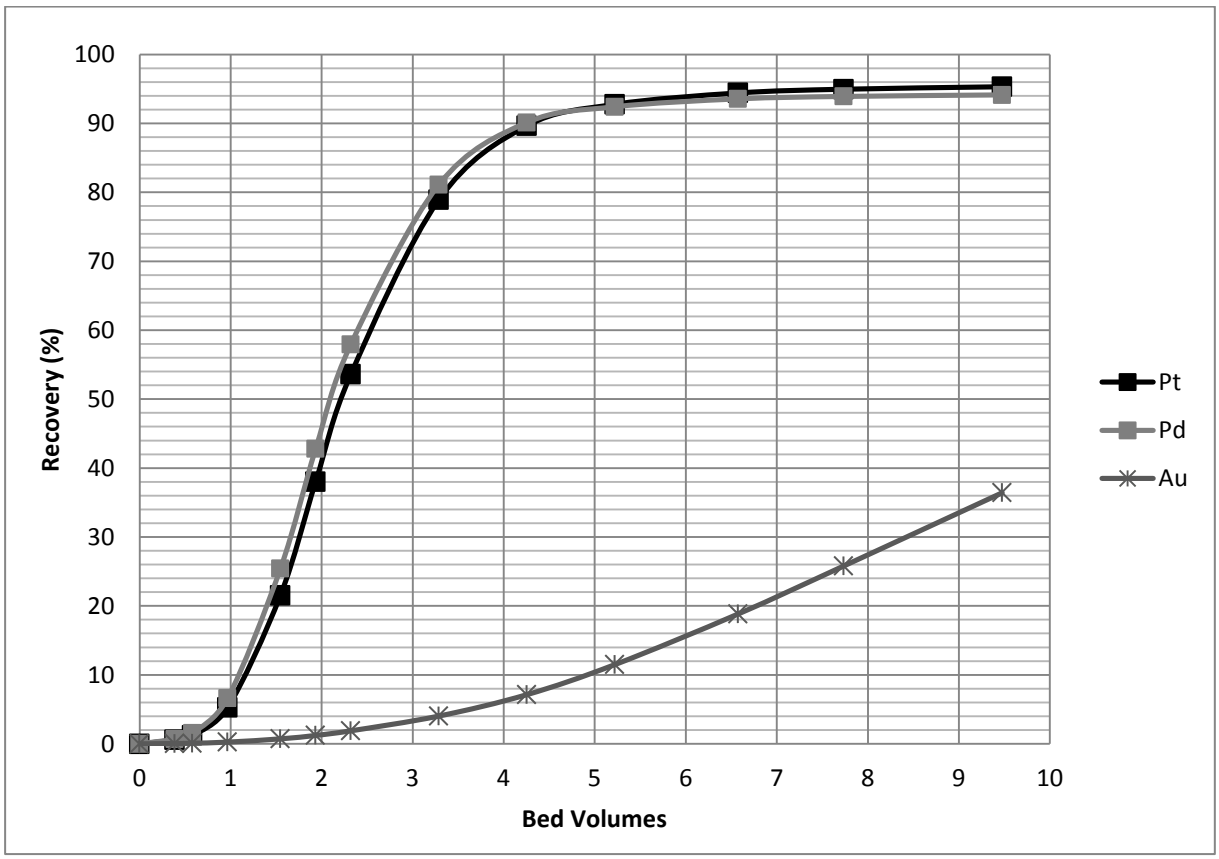
Date	28-Nov
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	3
Volume (mL)	40
Stirred (min)	30
pH	12.72
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.93
Flow rate (BV/hr)	2.3

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	S1	nd	0.58	16080.00	nd	nd					
water	S2	0.02	0.01	0.66	nd	nd					
	S3	0.77	0.83	2707.00	10.61	10.71	5.7	09:45	09:56	11	2.22
	S4	0.94	1.35	6352.00	16.47	14.84	5.7	09:56	10:02	6	4.07
	S5	2.11	1.00	2926.00	62.08	60.65	5.9	10:02	10:12	10	2.53
	S6	3.95	0.80	1203.00	132.90	143.90	5.7	10:12	10:23	11	2.22
	S7	5.60	0.43	686.20	137.40	166.60	6.1	10:23	10:36	13	2.01
	S8	7.35	0.21	467.70	98.42	127.00	5.6	10:36	10:46	10	2.40
	S9	9.06	0.09	302.10	45.65	63.82	5.4	10:57	11:10	13	1.78
	S10	14.81	0.04	176.80	10.42	16.99	6.5	11:23	11:34	12	2.32
	S11	18.70	0.05	131.50	3.77	6.46	5.3	11:50	12:00	10	2.27
	S12	21.59	0.02	105.40	1.31	2.40	6.1		12:33		
	S13	22.99	0.02	88.25	0.54	1.02	5.4	12:54	13:06	12	1.93
	S14	22.35	0.02	78.67	0.23	0.47	6.2	13:34	13:49	15	1.77
bulk	S15	18.96	0.05	129.60	7.78	11.63	6.6				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.00
5.41	0.39	0.04	0.68	0.03	0.57	0.00	0.04
8.12	0.58	0.21	1.55	0.20	1.25	0.01	0.08
13.54	0.97	0.79	6.60	0.83	5.25	0.02	0.24
21.66	1.55	0.73	25.41	0.84	21.54	0.03	0.72
27.07	1.93	0.64	42.79	0.79	38.02	0.04	1.21
32.49	2.32	0.98	57.96	1.29	53.61	0.11	1.89
46.02	3.29	0.38	81.12	0.55	78.93	0.16	4.02
59.56	4.25	0.10	90.13	0.16	89.66	0.23	7.13
73.10	5.22	0.05	92.41	0.08	92.77	0.38	11.49
92.05	6.57	0.01	93.56	0.03	94.41	0.36	18.83
108.29	7.74	0.01	93.91	0.02	94.96	0.55	25.80
132.66	9.48		94.13		95.32		36.42
Sum		**3.96**		**4.86**		**1.89**	



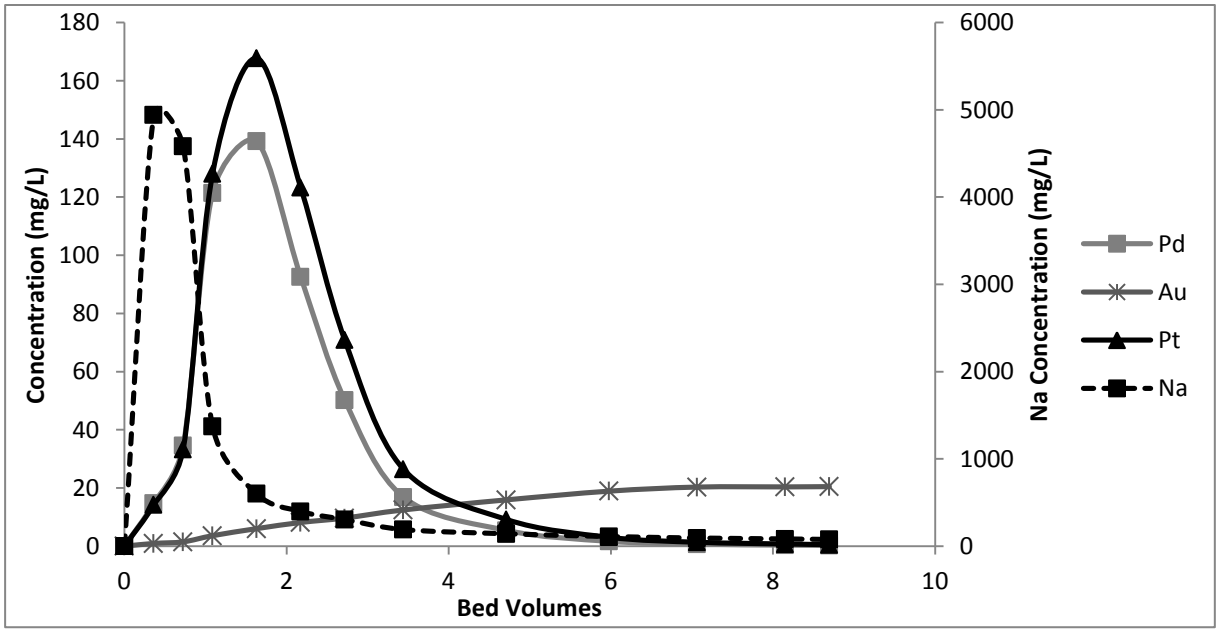
Elution experiment T

Loading experiment D

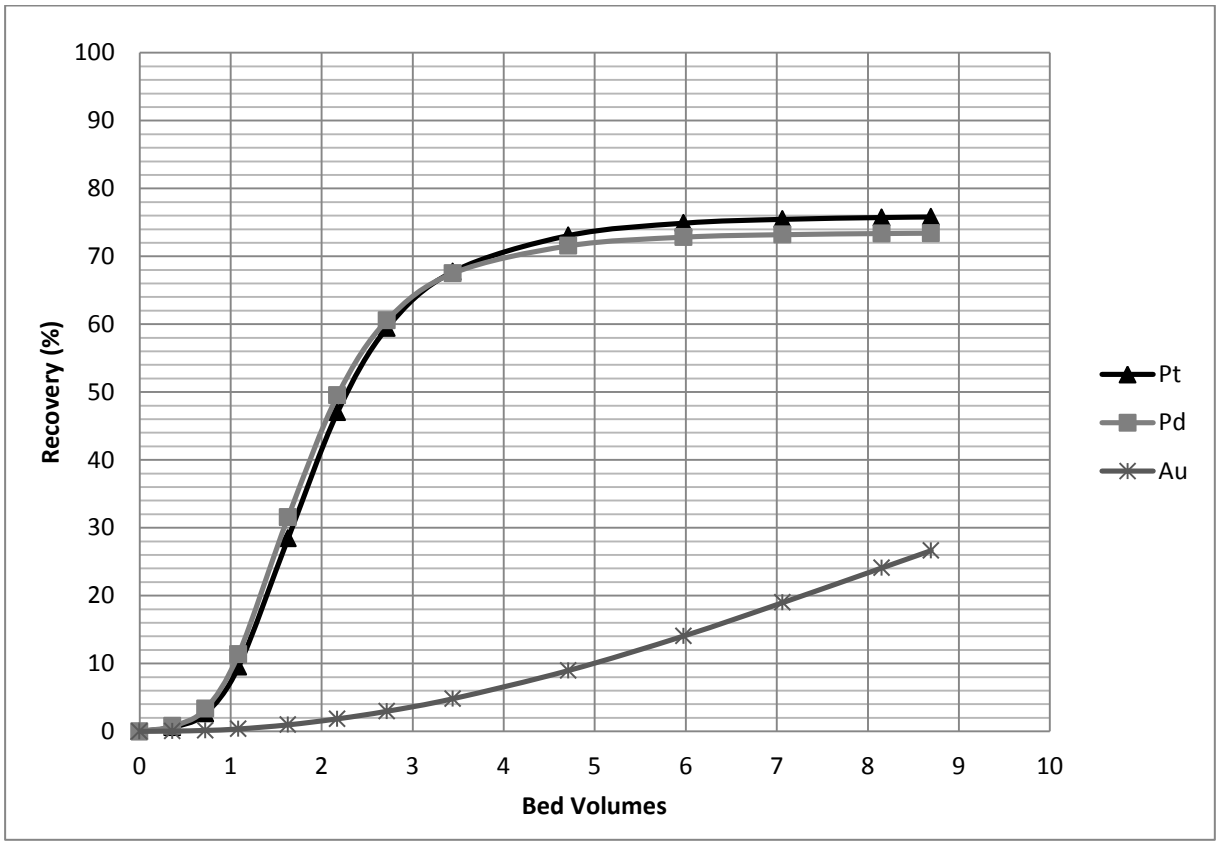
Date	28-Nov
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	4
Volume (mL)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	12
pH after	10.5
Flow rate (BV/hr)	2.4

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	T1	nd	0.48	17450.00	nd	nd					
water	T2	0.00	0.02	0.79	nd	nd					
	T3	0.94	1.02	4943.00	14.77	14.22	6.1	10:52	10:59	7	4.36
	T4	1.49	1.08	4583.00	34.62	33.32	5.5	10:59	11:08	9	3.06
	T5	3.60	0.98	1374.00	121.40	128.00	5.7	11:08	11:21	13	2.19
	T6	6.02	0.41	601.00	139.20	167.70	6	11:22	11:35	13	2.31
	T7	8.15	0.18	397.60	92.61	123.30	5.5	11:35	11:49	14	1.96
	T8	9.66	0.10	304.90	50.23	70.88	5.5	11:49	12:03	14	1.96
	T9	12.45	0.05	190.30	16.88	26.45	5.3	12:14	12:27	13	2.04
	T10	15.91	0.04	142.00	5.44	9.20	6	12:44	12:59	15	2.00
	T11	18.91	0.03	110.70	1.67	3.07	5.6	13:21	13:35	14	2.00
	T12	20.31	0.03	93.53	0.71	1.35	6		14:06		
	T13	20.38	0.02	82.85	0.37	0.75	6.5	14:16	14:33	17	1.91
	T14	20.47	0.02	76.93	0.26	0.51	5.5	14:35	14:48	13	2.12
bulk	T15	14.96	0.06	100.50	4.82	7.68	7.6				#DIV/0!



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.00
4.35	0.36	0.11	0.76	0.10	0.61	0.01	0.04
8.70	0.72	0.34	3.31	0.35	2.63	0.01	0.14
13.04	1.09	0.85	11.37	0.96	9.51	0.03	0.35
19.57	1.63	0.76	31.56	0.95	28.42	0.05	0.96
26.09	2.17	0.47	49.51	0.63	47.02	0.06	1.85
32.61	2.72	0.29	60.58	0.42	59.44	0.10	2.96
41.31	3.44	0.17	67.51	0.27	67.74	0.22	4.81
56.52	4.71	0.05	71.54	0.09	73.06	0.26	8.96
71.74	5.98	0.02	72.82	0.03	74.89	0.26	14.06
84.79	7.07	0.01	73.19	0.01	75.45	0.27	18.98
97.83	8.15	0.00	73.36	0.00	75.72	0.13	24.08
104.35	8.70		73.41		75.80		26.64
Sum		**3.09**		**3.87**		**1.39**	



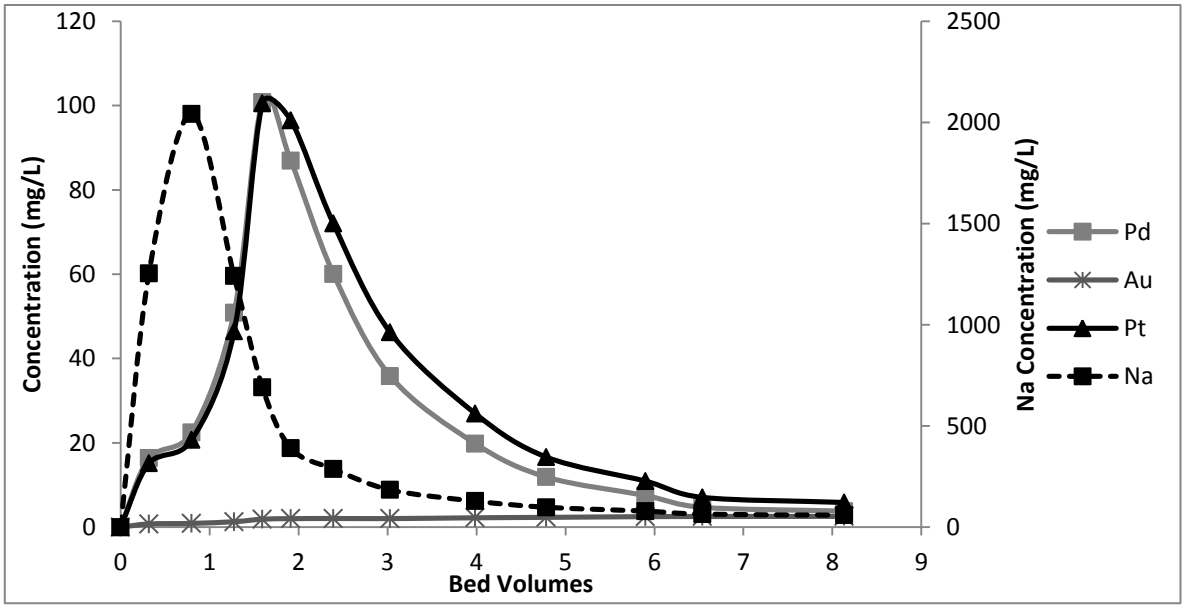
Elution experiment U

Loading experiment D

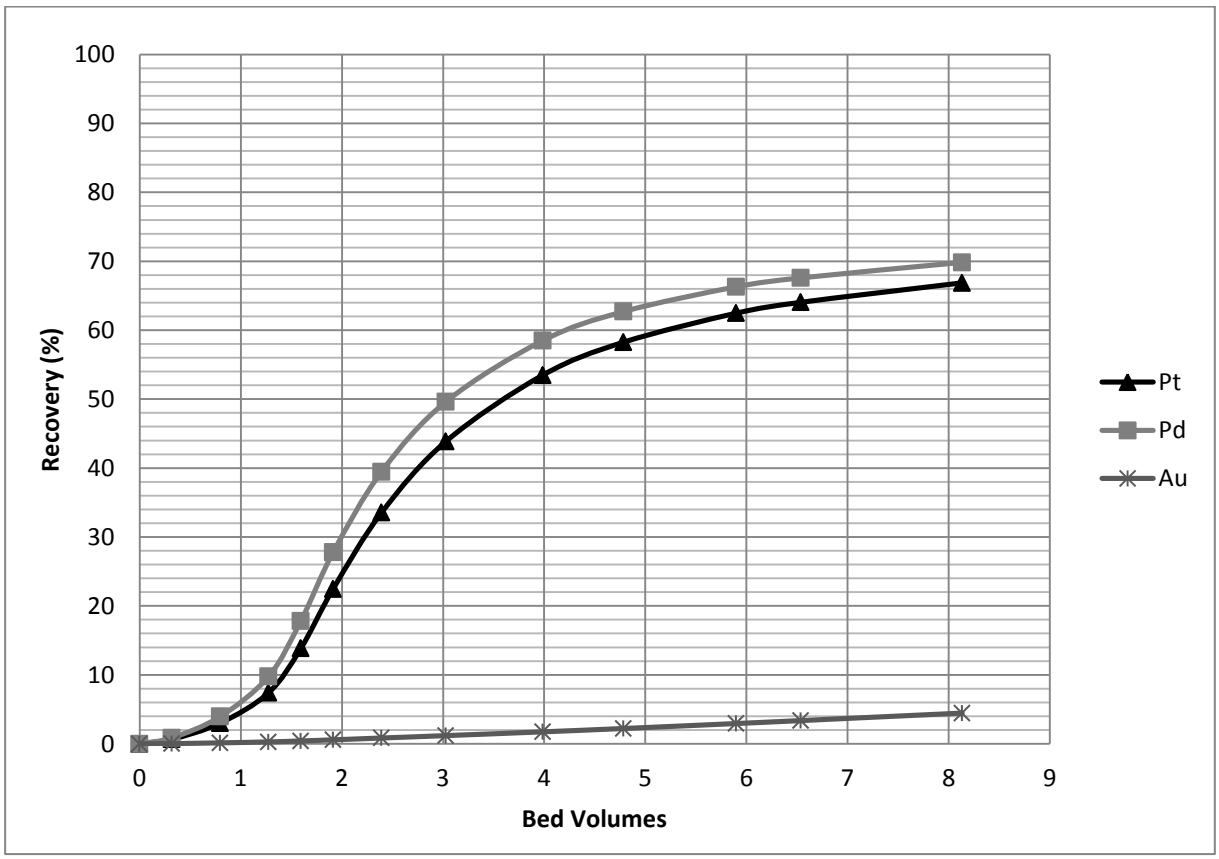
Date	29-Nov
Pre-treatment step	
NaOH (%)	1.1
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	13.45
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.44
Flow rate (BV/hr)	1.9

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	U1	nd	nd	6194.00	nd	nd					
water	U2	nd	0.02	0.65	nd	nd					
	U3	0.75	0.03	1254.00	16.36	15.13	5	09:09	09:21	12	1.79
	U4	0.88	nd	2041.00	22.44	20.67	5.6	09:21	09:36	15	1.60
	U5	1.28	nd	1241.00	50.88	46.42	5.1	09:36	09:51	15	1.46
	U6	1.88	nd	690.80	100.80	100.50	5.7	09:51	10:00	9	2.71
	U7	2.00	0.02	390.80	86.91	96.50	5.5	10:00	10:11	11	2.14
	U8	2.05	nd	287.40	60.07	72.00	6	10:11	10:23	12	2.14
	U9	2.02	nd	184.00	35.84	46.21	5.5	10:32	10:44	12	1.96
	U10	2.22	nd	128.30	19.81	26.93	5.8	11:00	11:13	13	1.91
	U11	2.31	nd	98.11	11.89	16.62	6.4	11:28	11:42	14	1.96
	U12	2.48	nd	78.95	7.49	10.91	6.6	12:00	12:15	15	1.89
	U13	2.52	nd	64.22	4.70	7.06	6	12:35	12:50	15	1.71
	U14	2.55	nd	59.03	3.79	5.85	5.5	13:09	13:23	14	1.68
bulk	U15	2.60	0.01	91.53	12.42	17.03	7				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.03	0.00	0.00	0.00
4.46	0.32	0.13	0.87	0.12	0.66	0.01	0.03
11.16	0.80	0.25	3.95	0.22	3.01	0.01	0.14
17.86	1.28	0.34	9.79	0.33	7.42	0.01	0.28
22.32	1.59	0.42	17.83	0.44	13.85	0.01	0.41
26.79	1.91	0.49	27.78	0.56	22.47	0.01	0.58
33.49	2.39	0.43	39.47	0.53	33.54	0.02	0.84
42.42	3.03	0.37	49.64	0.49	43.88	0.03	1.19
55.81	3.99	0.18	58.50	0.24	53.49	0.03	1.73
66.97	4.78	0.15	62.70	0.22	58.26	0.04	2.22
82.60	5.90	0.05	66.30	0.08	62.47	0.02	2.94
91.53	6.54	0.09	67.59	0.14	64.05	0.06	3.37
113.85	8.13		69.84		66.87		4.46
Sum		**2.94**		**3.41**		**0.23**	



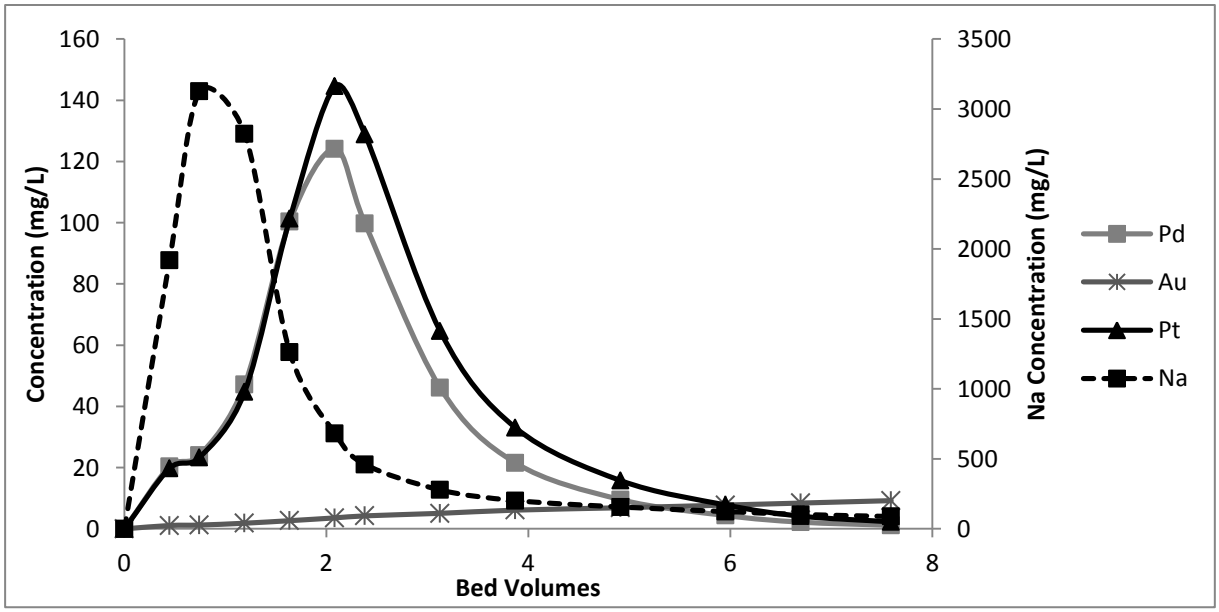
Elution experiment V

Loading experiment D

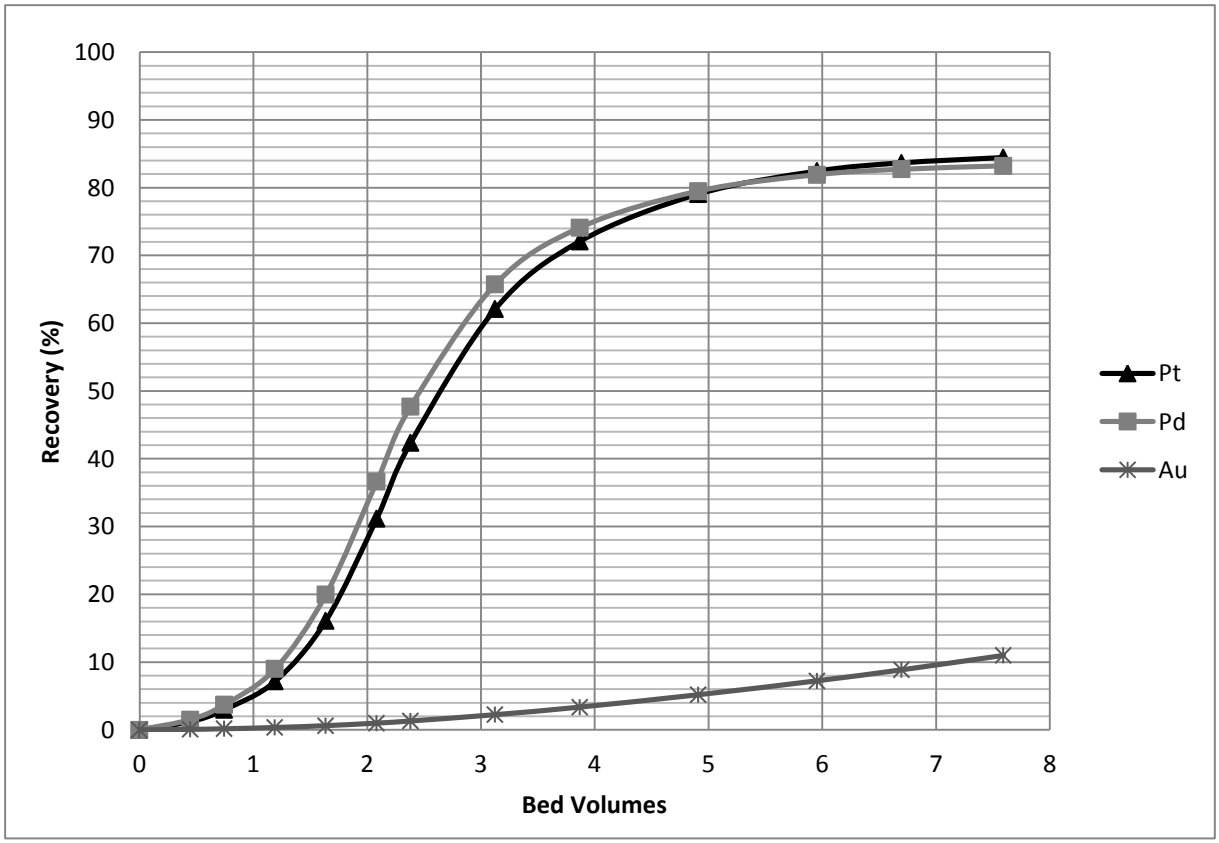
Date	29-Nov
Pre-treatment step	
NaOH (%)	1.1
NaCN (%)	1
Volume (mL)	40
Stirred (min)	30
pH	13.45
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.77
Flow rate (BV/hr)	1.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	V1	nd	0.51	10660.00	nd	nd					
water	V2	0.02	0.03	0.66	nd	nd					
	V3	1.09	1.29	1919.00	20.34	19.76	5	10:07	10:18	11	1.95
	V4	1.24	1.77	3127.00	24.02	23.36	5.9	10:18	10:32	14	1.81
	V5	1.84	1.77	2822.00	47.19	44.80	5	10:32	10:44	12	1.79
	V6	2.67	0.71	1262.00	100.40	101.30	6.3	10:44	10:59	15	1.80
	V7	3.58	0.25	681.60	124.10	144.60	6	10:59	11:13	14	1.84
	V8	4.24	0.11	460.70	99.75	128.80	5	11:13	11:25	12	1.79
	V9	5.07	0.05	278.10	46.06	64.58	5.6	11:37	11:50	13	1.85
	V10	6.12	0.03	202.30	21.56	33.07	6.4	12:00	12:15	15	1.83
	V11	6.89	0.03	156.20	9.54	15.77	5.2	12:35	12:51	16	1.39
	V12	7.77	0.02	123.50	4.35	7.80	5.1	13:09	13:23	14	1.56
	V13	8.42	0.01	102.70	2.18	4.14	5	13:37	13:51	14	1.53
	V14	9.22	0.01	88.47	1.15	2.29	5.4	14:08	14:18	10	2.31
bulk	V15	8.07	0.04	157.60	14.75	22.14	6.6				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.06	**0.00**	0.06	0.00	0.00	0.00
6.25	0.45	0.09	1.51	0.09	1.21	0.00	0.07
10.42	0.74	0.22	3.71	0.21	2.97	0.01	0.16
16.67	1.19	0.46	8.99	0.46	7.15	0.01	0.34
22.92	1.64	0.70	19.95	0.77	16.11	0.02	0.62
29.18	2.08	0.47	36.62	0.57	31.18	0.02	0.99
33.34	2.38	0.76	47.70	1.01	42.35	0.05	1.30
43.77	3.13	0.35	65.75	0.51	62.11	0.06	2.24
54.19	3.87	0.23	74.12	0.36	72.08	0.09	3.36
68.77	4.91	0.10	79.51	0.17	79.07	0.11	5.18
83.36	5.95	0.03	81.91	0.06	82.44	0.08	7.24
93.78	6.70	0.02	82.72	0.04	83.66	0.11	8.86
106.29	7.59		83.22		84.45		10.98
Sum		**3.50**		**4.31**		**0.57**	



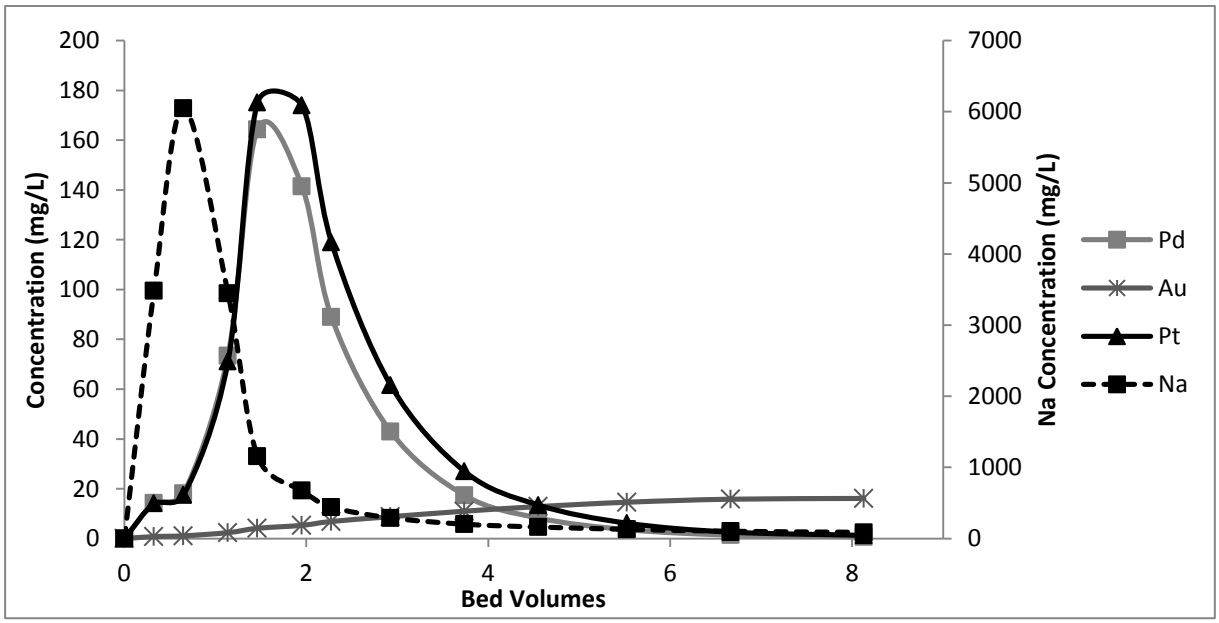
Elution experiment W

Loading experiment D

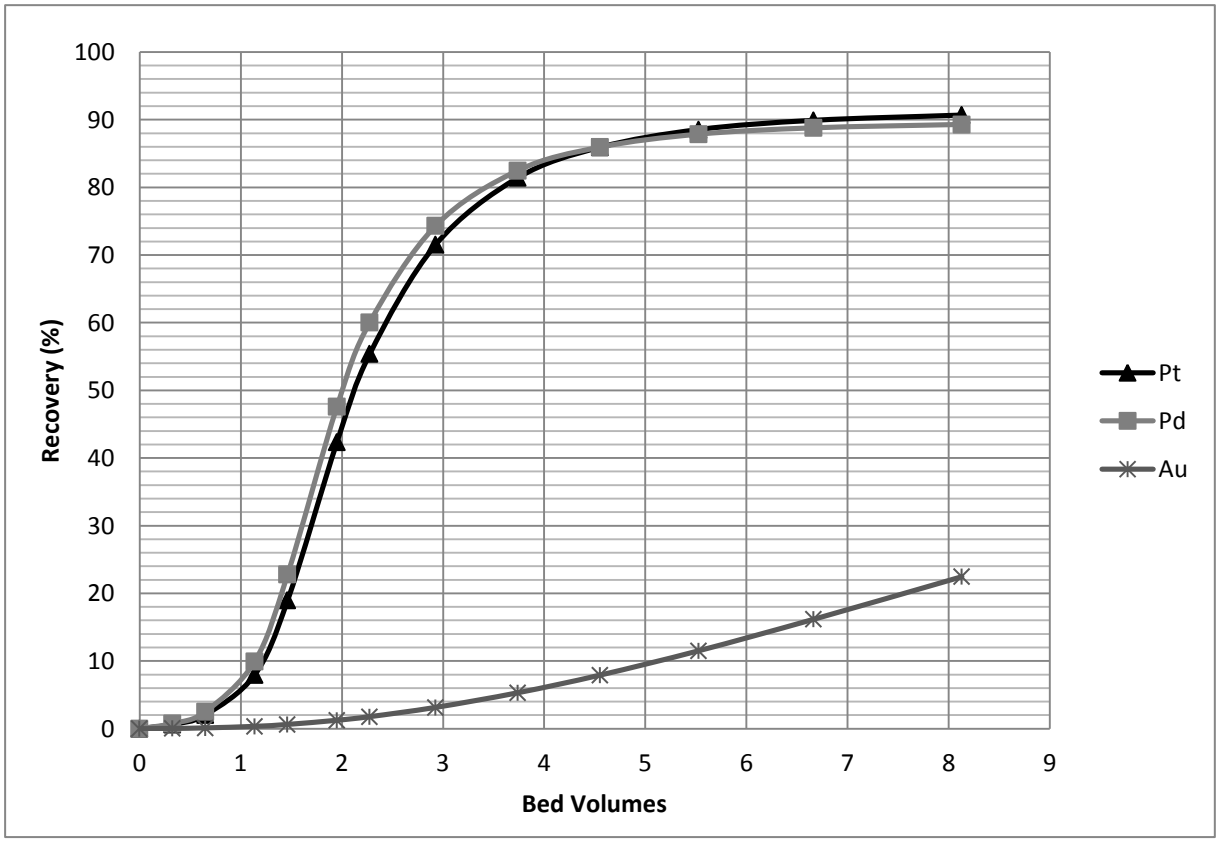
Date	30-Nov
Pre-treatment step	
NaOH (%)	1.1
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.36
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.85
Flow rate (BV/hr)	2.0

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	W1	nd	0.56	13600.00	nd	nd					
water	W2	nd	0.01	0.60	nd	nd					
	W3	0.78	1.03	3483.00	14.24	14.13	5.6	08:46	08:53	7	3.43
	W4	1.09	1.64	6049.00	18.15	17.49	5.4	08:53	09:04	11	2.10
	W5	2.37	1.81	3450.00	73.45	71.06	5.6	09:04	09:18	14	1.71
	W6	4.11	0.74	1155.00	164.30	175.10	5	09:18	09:30	12	1.79
	W7	5.30	0.30	676.10	141.50	174.00	5.7	09:30	09:45	15	1.63
	W8	6.87	0.14	442.60	88.96	119.00	5.5	09:45	09:56	11	2.14
	W9	8.78	0.07	290.20	42.98	61.65	5.5	10:02	10:14	12	1.96
	W10	10.99	0.05	201.20	17.37	26.96	5	10:28	10:40	12	1.79
	W11	12.83	0.03	161.70	8.23	13.43	5.6	10:53	11:07	14	1.71
	W12	14.59	0.02	129.20	3.56	6.16	5.4	11:24	11:37	13	1.78
	W13	15.80	0.02	102.40	1.40	2.57	5.1	12:00	12:12	12	1.82
	W14	16.11	0.01	87.75	0.65	1.28	5.4	12:40	12:55	15	1.54
bulk	W15	13.94	0.04	140.10	9.34	14.26	8.4				



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)	Na (mg)
0.00	0.00	0.03	**0.00**	0.03	0.00	0.00	0.00	7.93
4.55	0.33	0.07	0.77	0.07	0.63	0.00	0.03	21.70
9.10	0.65	0.31	2.52	0.30	2.04	0.01	0.12	32.43
15.93	1.14	0.54	9.95	0.56	7.97	0.01	0.34	10.48
20.49	1.46	1.04	22.80	1.19	18.96	0.03	0.63	6.25
27.31	1.95	0.52	47.61	0.67	42.33	0.03	1.25	2.55
31.87	2.28	0.60	60.07	0.82	55.41	0.07	1.78	3.34
40.97	2.93	0.34	74.33	0.50	71.53	0.11	3.15	2.80
52.35	3.74	0.15	82.49	0.23	81.42	0.14	5.31	2.07
63.73	4.55	0.08	85.95	0.13	85.92	0.19	7.92	1.99
77.39	5.53	0.04	87.86	0.07	88.55	0.24	11.52	1.85
93.33	6.67	0.02	88.80	0.04	89.91	0.33	16.17	1.95
113.81	8.13		89.30		90.68		22.46	
Sum		**3.76**		**4.62**		**1.17**		**95.32**



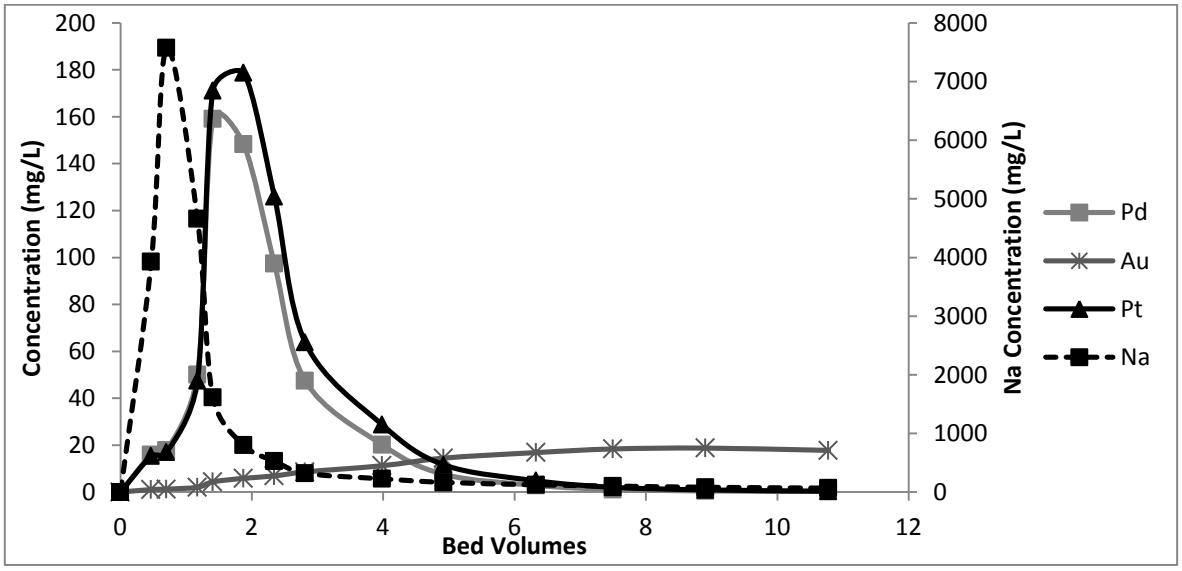
Elution experiment X

Loading experiment D

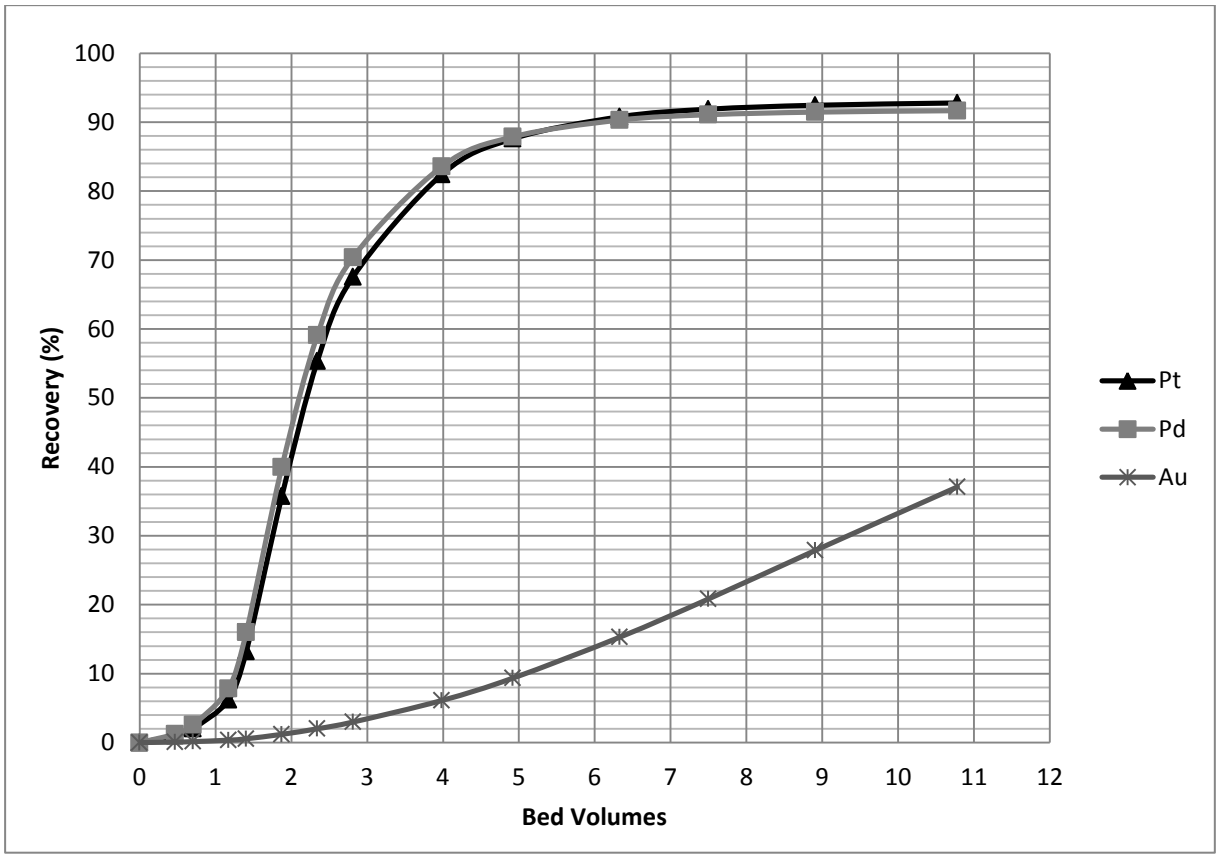
Date	30-Nov
Pre-treatment step	
NaOH (%)	1.1
NaCN (%)	3
Volume (mL)	40
Stirred (min)	30
pH	13.31
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11
Flow rate (BV/hr)	2.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	X1	nd	0.66	18860.00	nd	nd					
water	X2	0.02	0.02	0.71	nd	nd					
	X3	1.07	1.12	3930.00	15.93	15.38	6	09:39	09:49	10	2.57
	X4	1.26	1.53	7575.00	17.79	16.98	5.9	09:49	09:56	7	3.61
	X5	2.05	1.28	4661.00	50.04	47.49	5	09:56	10:03	9	2.38
	X6	4.36	0.89	1616.00	159.10	171.10	5.4	10:03	10:11	8	2.89
	X7	5.86	0.40	802.80	148.30	178.80	5.4	10:11	10:19	7	3.31
	X8	6.90	0.20	527.90	97.35	126.00	6	10:19	10:28	9	2.86
	X9	8.60	0.09	320.20	47.48	63.78	5.2	10:34	10:42	8	2.79
	X10	11.24	0.05	226.60	20.16	28.72	6.1	10:53	11:03	10	2.61
	X11	14.48	0.04	165.30	7.55	11.61	5.6	11:18	11:27	9	2.67
	X12	16.84	0.03	124.20	2.84	4.84	5.6	11:44	11:53	9	2.67
	X13	18.39	0.02	102.90	1.13	2.04	5	12:13	12:21	8	2.68
	X14	18.75	0.02	82.09	0.49	0.93	5.7	12:42	12:51	9	2.71
	X15	17.77	0.01	67.71	0.18	0.37	5.3	13:22	13:30	8	2.84
bulk	X16	15.65	0.06	130.00	7.80	11.03	6.5				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.05	0.00	0.05	0.00	0.00	0.00
6.56	0.47	0.06	1.24	0.05	0.99	0.00	0.07
9.84	0.70	0.22	2.56	0.21	2.03	0.01	0.14
16.40	1.17	0.34	7.84	0.36	6.18	0.01	0.35
19.69	1.41	1.01	15.99	1.15	13.21	0.03	0.55
26.25	1.87	0.81	39.95	1.00	35.72	0.04	1.20
32.81	2.34	0.48	59.09	0.62	55.33	0.05	2.00
39.37	2.81	0.55	70.38	0.76	67.54	0.16	2.98
55.78	3.98	0.18	83.56	0.26	82.41	0.17	6.11
68.90	4.92	0.10	87.88	0.16	87.60	0.31	9.35
88.59	6.33	0.03	90.30	0.06	90.78	0.29	15.28
104.99	7.50	0.02	91.08	0.03	91.88	0.37	20.84
124.68	8.91	0.01	91.46	0.02	92.45	0.48	27.87
150.92	10.78		91.67		92.79		37.09
Sum		**3.86**		**4.73**		**1.93**	



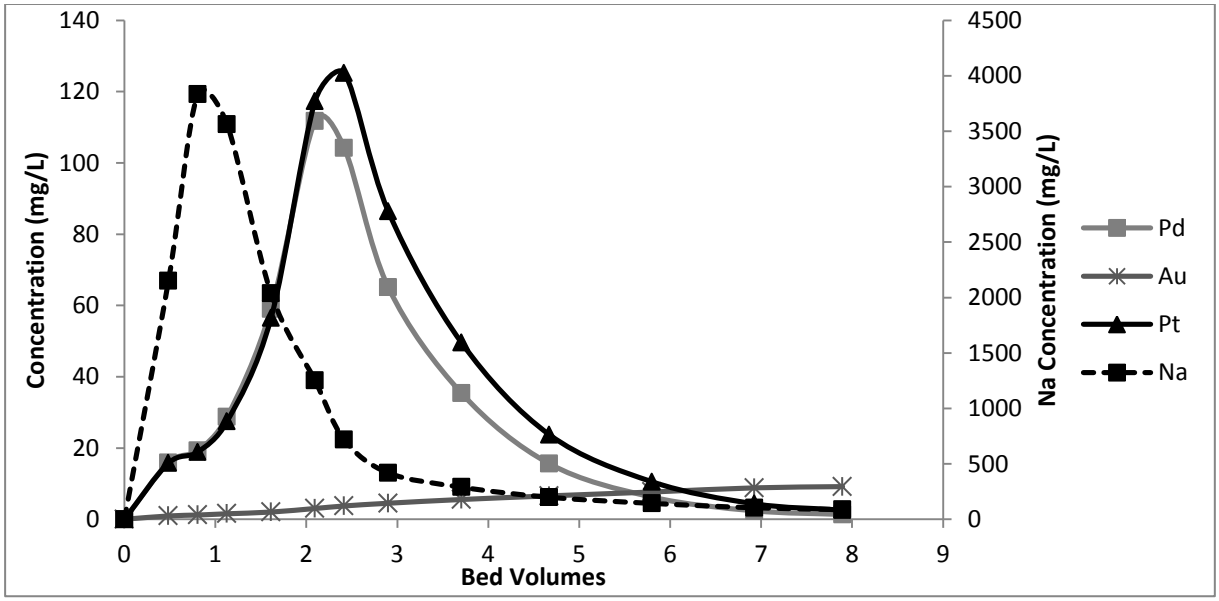
Elution experiment Y

Loading experiment D

Date	06-Dec
Pre-treatment step	
NaOH (%)	1.65
NaCN (%)	1
Volume (mL)	40
Stirred (min)	30
pH	13.61
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.78
Flow rate (BV/hr)	1.9

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	Y1	nd	0.46	13430.00	nd	nd					
water	Y2	0.02	0.01	1.34	nd	nd					
	Y3	0.93	0.96	2149.00	15.89	15.75	5.5	09:12	09:24	12	1.96
	Y4	1.19	1.46	3834.00	19.28	18.87	4.9	09:24	09:34	10	2.10
	Y5	1.54	1.41	3563.00	28.74	27.45	5.2	09:34	09:47	13	1.71
	Y6	2.02	0.85	2039.00	58.96	56.46	5.4	09:47	10:01	14	1.65
	Y7	3.03	0.42	1252.00	111.70	117.30	5.4	10:01	10:13	12	1.93
	Y8	3.74	0.14	717.20	104.20	125.20	5.8	10:13	10:24	11	2.26
	Y9	4.50	0.07	418.50	65.11	86.42	5.3	10:30	10:41	11	2.06
	Y10	5.55	0.03	289.30	35.38	49.56	5.4	10:51	11:03	12	1.93
	Y11	6.56	0.02	198.20	15.57	23.72	5.3	11:22	11:35	13	1.75
	Y12	7.65	0.02	143.20	6.22	10.52	5	11:58	12:09	11	1.95
	Y13	8.82	0.01	103.50	2.37	4.33	5.5	12:35	12:47	12	1.96
	Y14	9.16	0.02	87.44	1.35	2.56	5.4	13:01	13:13	12	1.93
bulk	Y15	7.67	0.03	176.10	15.36	21.99					



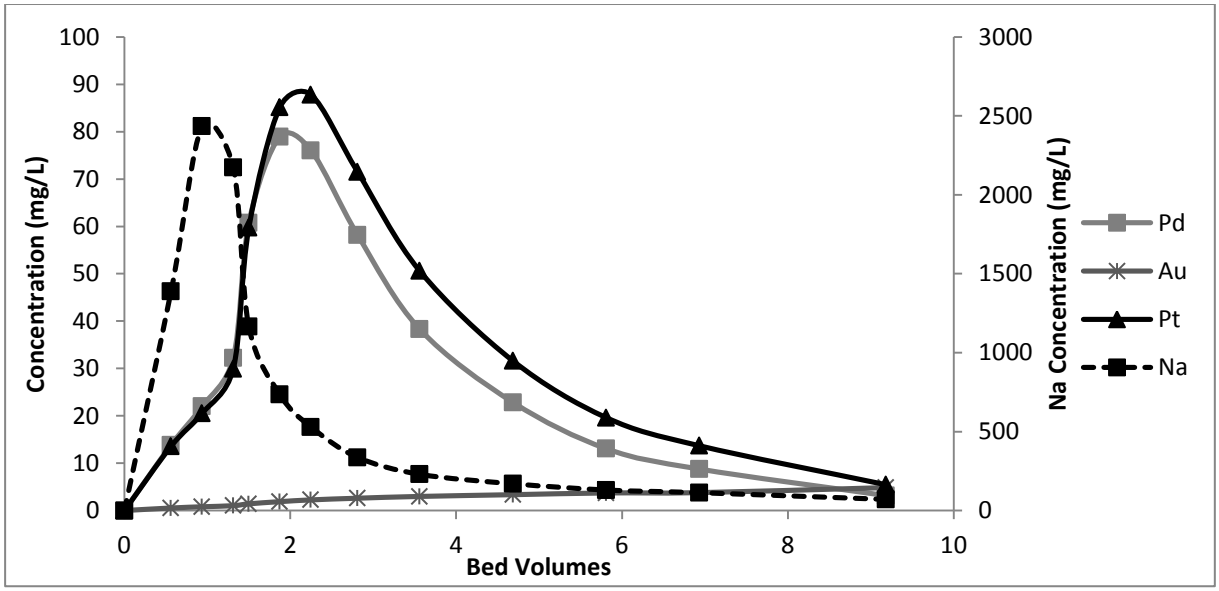
Elution experiment Z

Loading experiment D

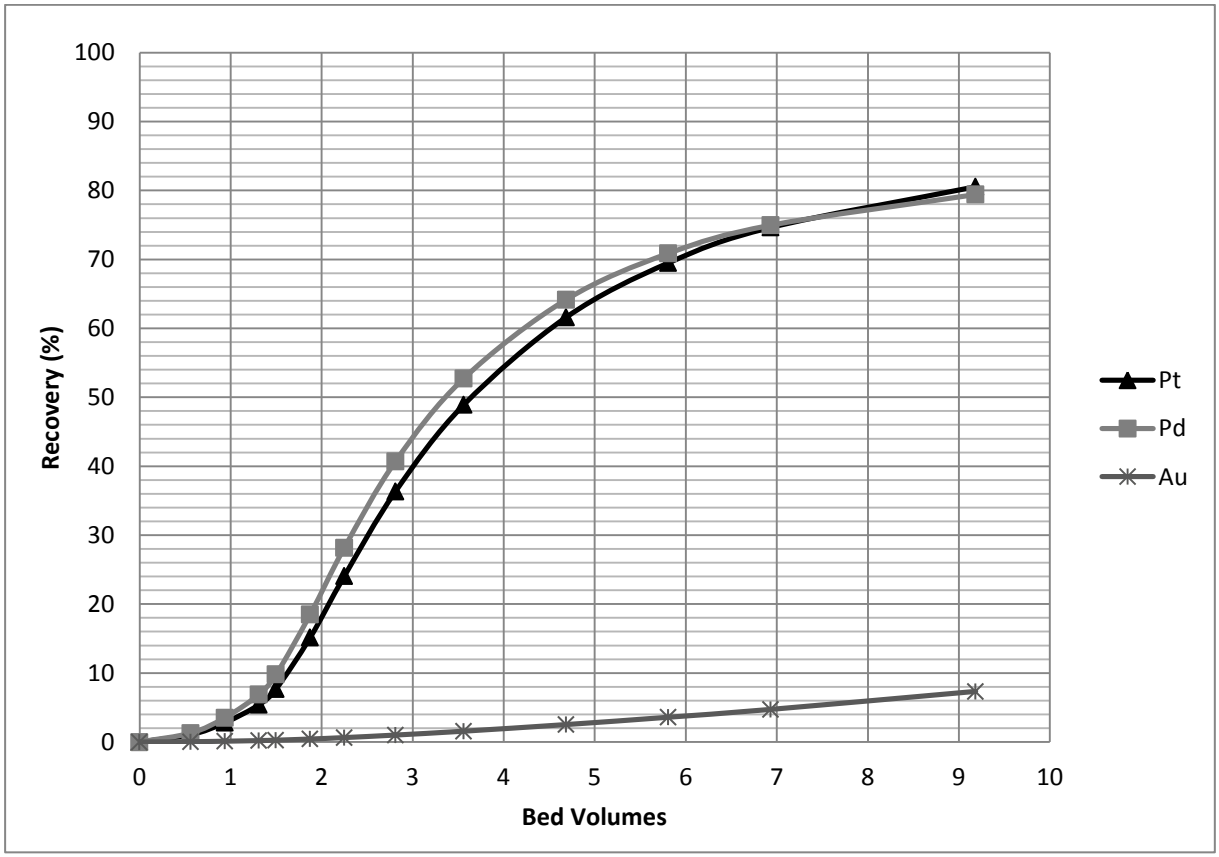
Date	06-Dec
Pre-treatment step	
NaOH (%)	1.65
NaCN (%)	0
Volume (mL)	40
Stirred (min)	30
pH	13.63
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	10.75
Flow rate (BV/hr)	2.2

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	Z1	nd	0.08	8723.00	nd	nd					
water	Z2	nd	0.01	1.59	nd	nd					
	Z3	0.54	0.25	1389.00	13.85	13.58	5	10:00	10:13	13	1.65
	Z4	0.80	0.18	2434.00	21.99	20.54	5.3	10:13	10:25	12	1.89
	Z5	1.02	0.16	2174.00	32.22	29.94	5.4	10:25	10:33	8	2.89
	Z6	1.41	0.10	1165.00	60.75	59.70	6	10:33	10:42	9	2.86
	Z7	1.88	0.06	735.00	78.96	85.17	5.1	10:42	10:49	7	3.12
	Z8	2.25	0.03	529.40	76.04	87.81	5.5	10:49	10:58	9	2.62
	Z9	2.60	0.02	336.70	58.17	71.51	5.3	11:04	11:13	9	2.52
	Z10	2.98	0.01	229.60	38.28	50.58	5.5	11:23	11:34	11	2.14
	Z11	3.35	0.01	169.50	22.83	31.58	5.5	11:51	12:03	12	1.96
	Z12	3.71	0.01	129.90	13.06	19.61	5.2	12:23	12:35	12	1.86
	Z13	3.78	0.02	113.00	8.76	13.67	5.5	13:00	13:14	14	1.68
	Z14	4.84	0.01	70.56	3.15	5.45	5	13:52	14:04	12	1.79
bulk	Z15	4.13	0.01	132.50	16.09	22.36	7.9				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.05	0.00	0.05	0.00	0.00	0.00
7.87	0.56	0.09	1.29	0.09	1.05	0.00	0.04
13.12	0.94	0.14	3.53	0.13	2.80	0.00	0.11
18.37	1.31	0.12	6.91	0.12	5.40	0.00	0.20
20.99	1.50	0.37	9.80	0.38	7.71	0.01	0.26
26.24	1.87	0.41	18.51	0.45	15.16	0.01	0.43
31.49	2.25	0.53	28.17	0.63	24.06	0.02	0.64
39.36	2.81	0.51	40.72	0.64	36.36	0.03	1.00
49.86	3.56	0.48	52.74	0.65	48.92	0.05	1.57
65.60	4.69	0.28	64.17	0.40	61.60	0.06	2.52
81.35	5.81	0.17	70.88	0.26	69.50	0.06	3.59
97.09	6.93	0.19	74.96	0.30	74.64	0.14	4.73
128.58	9.18		79.41		80.54		7.34
Sum		**3.34**		**4.11**		**0.38**	



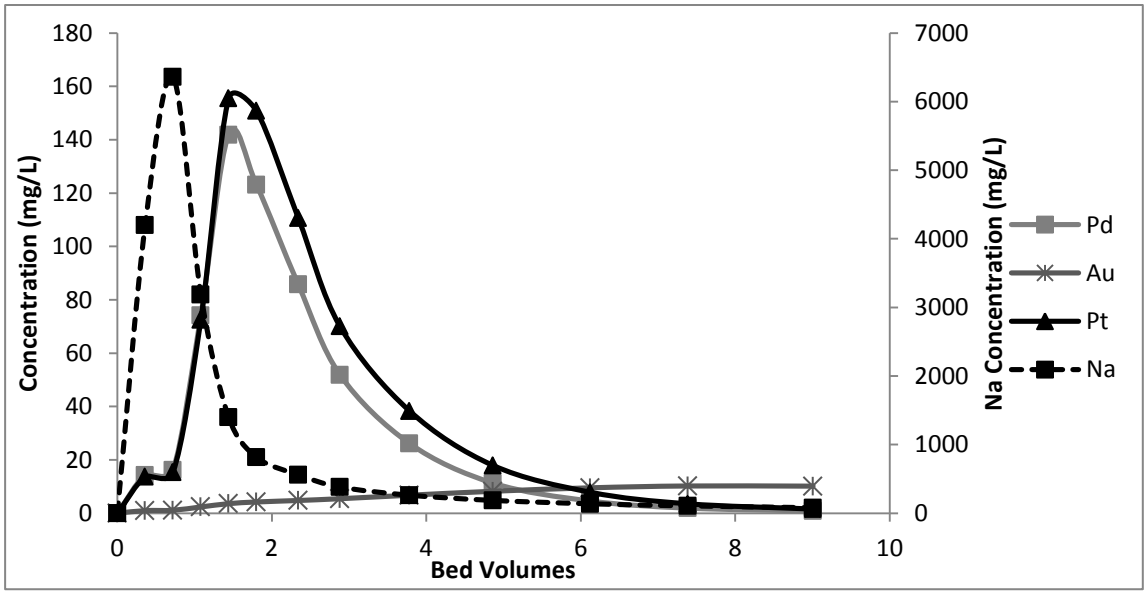
Elution experiment AA

Loading experiment D

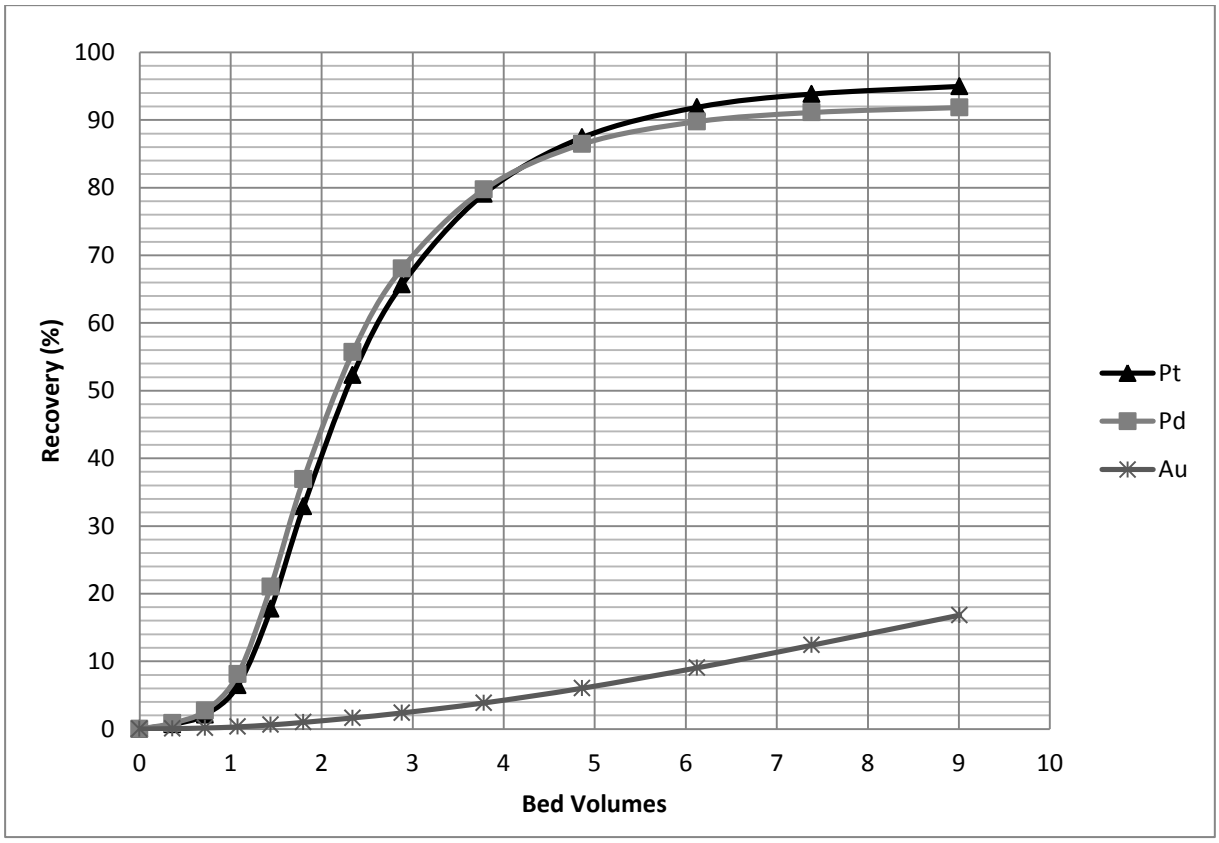
Date	08-Dec
Pre-treatment step	
NaOH (%)	1.65
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.71
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11.18
Flow rate (BV/hr)	2.2

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	AA1	nd	0.51	17270.00	nd	nd					
water	AA2	nd	0.01	1.65	nd	nd					
	AA3	0.96	1.10	4199.00	14.27	13.66	5.7	09:57	10:07	10	2.44
	AA4	1.11	1.56	6360.00	16.20	15.33	5.7	10:07	10:17	10	2.44
	AA5	2.35	1.31	3187.00	74.14	72.51	5.4	10:17	10:26	9	2.57
	AA6	3.57	0.63	1399.00	141.90	155.50	5.1	10:26	10:36	10	2.19
	AA7	4.21	0.25	815.80	123.10	150.80	6.2	10:36	10:48	12	2.21
	AA8	4.76	0.12	559.10	85.75	110.70	5.5	10:48	10:59	11	2.14
	AA9	5.43	0.06	381.30	51.86	70.04	6.1	11:04	11:17	13	2.01
	AA10	6.74	0.03	262.20	26.13	38.33	5.1	11:28	11:39	11	1.99
	AA11	8.22	0.02	186.30	11.27	17.90	6	11:55	12:08	13	1.98
	AA12	9.51	0.01	137.00	4.55	7.84	5.4	12:31	12:43	12	1.93
	AA13	10.20	0.01	106.40	1.90	3.52	5.3	13:07	13:19	12	1.89
	AA14	10.14	0.00	79.88	0.81	1.56	6.5	13:50	14:03	13	2.14
bulk	AA15	8.74	0.03	139.70	9.17	14.33	8.6				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.03	0.00	0.00	0.00
5.04	0.36	0.08	0.85	0.07	0.68	0.01	0.05
10.09	0.72	0.23	2.68	0.22	2.11	0.01	0.15
15.13	1.08	0.54	8.09	0.58	6.45	0.01	0.31
20.18	1.44	0.67	21.03	0.77	17.73	0.02	0.60
25.22	1.80	0.79	36.91	0.99	32.87	0.03	0.98
32.79	2.34	0.52	55.67	0.68	52.27	0.04	1.63
40.35	2.88	0.49	68.04	0.68	65.68	0.08	2.37
52.96	3.78	0.28	79.72	0.43	79.08	0.11	3.85
68.09	4.86	0.14	86.44	0.23	87.42	0.16	6.02
85.75	6.12	0.06	89.76	0.10	91.87	0.17	9.03
103.40	7.39	0.03	91.11	0.06	93.84	0.23	12.38
126.10	9.01		91.84		94.97		16.82
Sum		**3.87**		**4.84**		**0.87**	



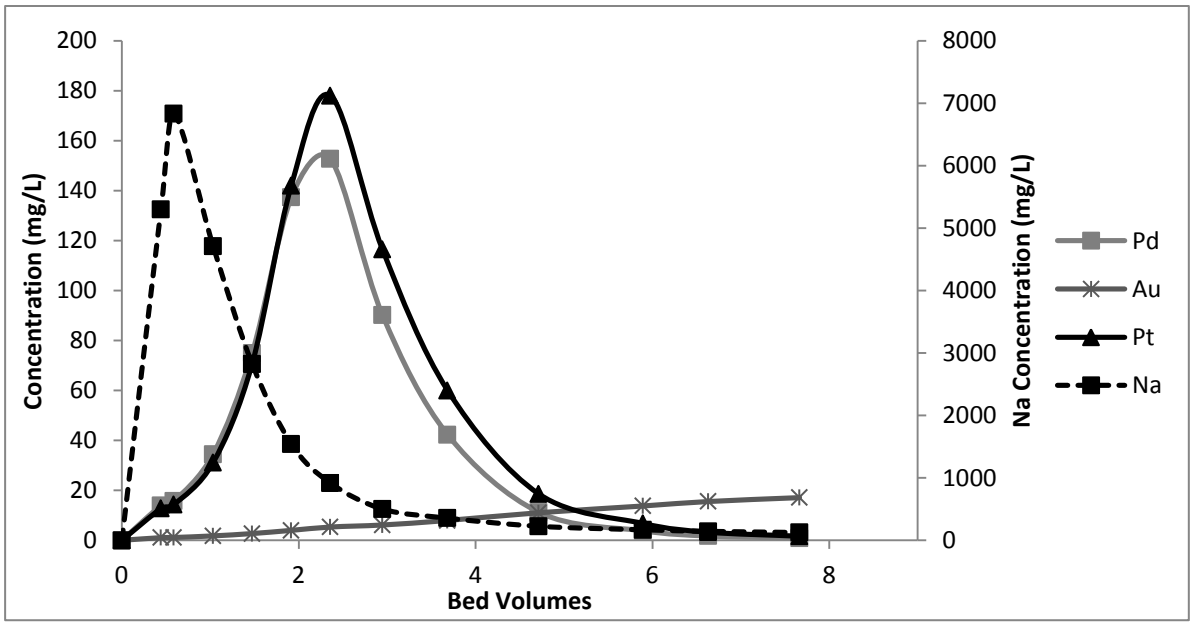
Elution experiment AB

Loading experiment D

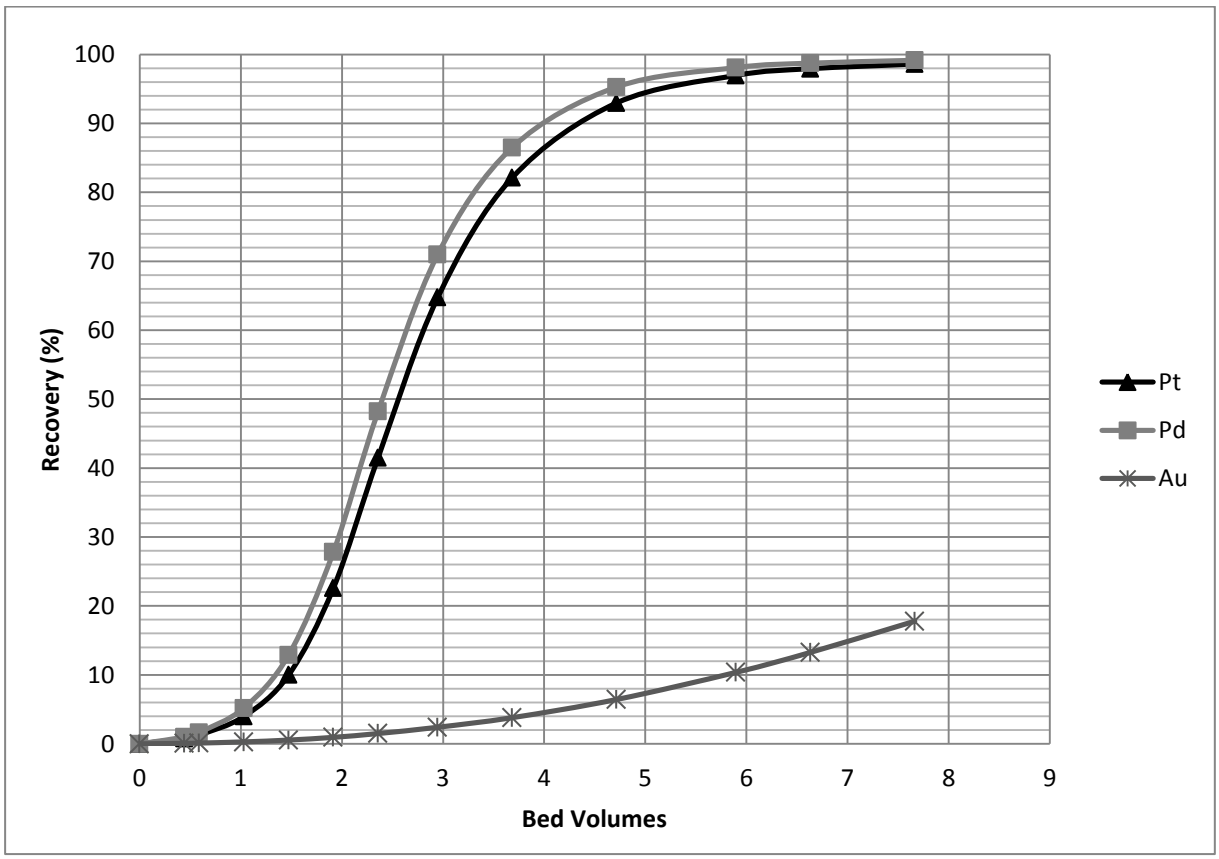
Date	08-Dec	
Pre-treatment step		**wt %**
NaOH (g)	0.66	1.65
NaCN (g)	1.2	3
Volume (mL)	40	
Stirred (min)	30	
pH	13.72	
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11.14
Flow rate (BV/hr)	1.8

	mg/L	Au	Cu	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	AB1	nd	0.66	21500.00	nd	nd					
water	AB2	nd	0.01	1.46	nd	nd					
	AB3	1.05	1.13	5301.00	13.89	12.71	6	10:53	11:03	10	2.57
	AB4	1.13	1.44	6830.00	15.68	14.32	5.1	11:03	11:12	9	2.43
	AB5	1.76	1.32	4711.00	34.46	31.09	5.1	11:12	11:25	13	1.68
	AB6	2.70	1.10	2824.00	74.96	70.70	5.1	11:25	11:38	13	1.68
	AB7	3.97	0.56	1543.00	137.30	142.00	5.6	11:38	11:53	15	1.60
	AB8	5.31	0.26	916.60	152.70	178.00	5.3	11:53	12:08	15	1.51
	AB9	6.12	0.07	500.30	90.15	116.40	5.3	12:14	12:30	16	1.42
	AB10	7.94	0.03	354.50	42.26	59.96	5.5	12:43	12:57	14	1.68
	AB11	11.03	0.01	224.00	11.21	18.53	6.3		13:32		
	AB12	13.73	0.01	168.20	3.78	6.74	6.5	13:51	14:08	17	1.64
	AB13	15.52	0.01	143.40	1.71	3.23	5.3	14:22	14:35	13	1.75
	AB14	17.08	0.01	124.70	0.83	1.63	5.9	14:51	15:08	17	1.49
bulk	AB15	12.93	0.03	199.90	16.37	23.73	6.5				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.04	0.00	0.00	0.00
6.19	0.44	0.03	0.98	0.03	0.75	0.00	0.06
8.25	0.59	0.16	1.67	0.14	1.29	0.01	0.11
14.44	1.03	0.34	5.20	0.32	3.97	0.01	0.28
20.63	1.47	0.66	12.89	0.66	9.99	0.02	0.54
26.82	1.92	0.90	27.82	0.99	22.58	0.03	0.94
33.01	2.36	1.00	48.22	1.21	41.51	0.05	1.49
41.27	2.95	0.68	70.99	0.91	64.74	0.07	2.40
51.58	3.68	0.39	86.51	0.57	82.13	0.14	3.79
66.02	4.72	0.12	95.28	0.21	92.97	0.20	6.43
82.53	5.90	0.03	98.10	0.05	96.96	0.15	10.36
92.85	6.63	0.02	98.74	0.04	97.94	0.24	13.26
107.29	7.66	0.04	99.16	0.07	98.61		17.79
Sum		**4.40**		**5.23**		**0.92**	



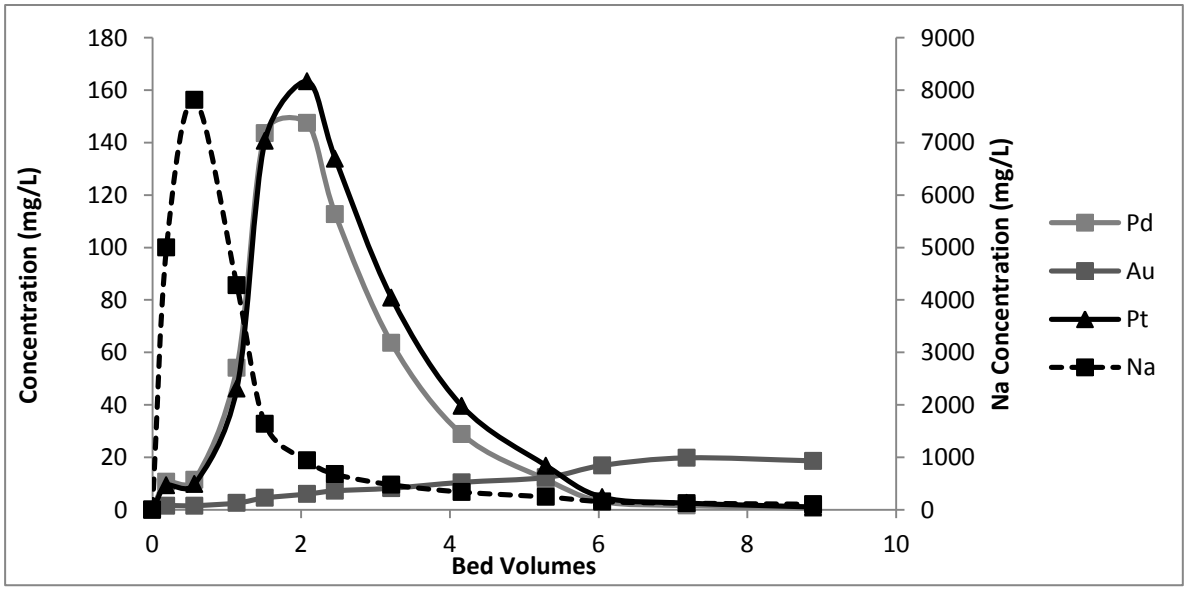
Elution experiment AC

Loading experiment D

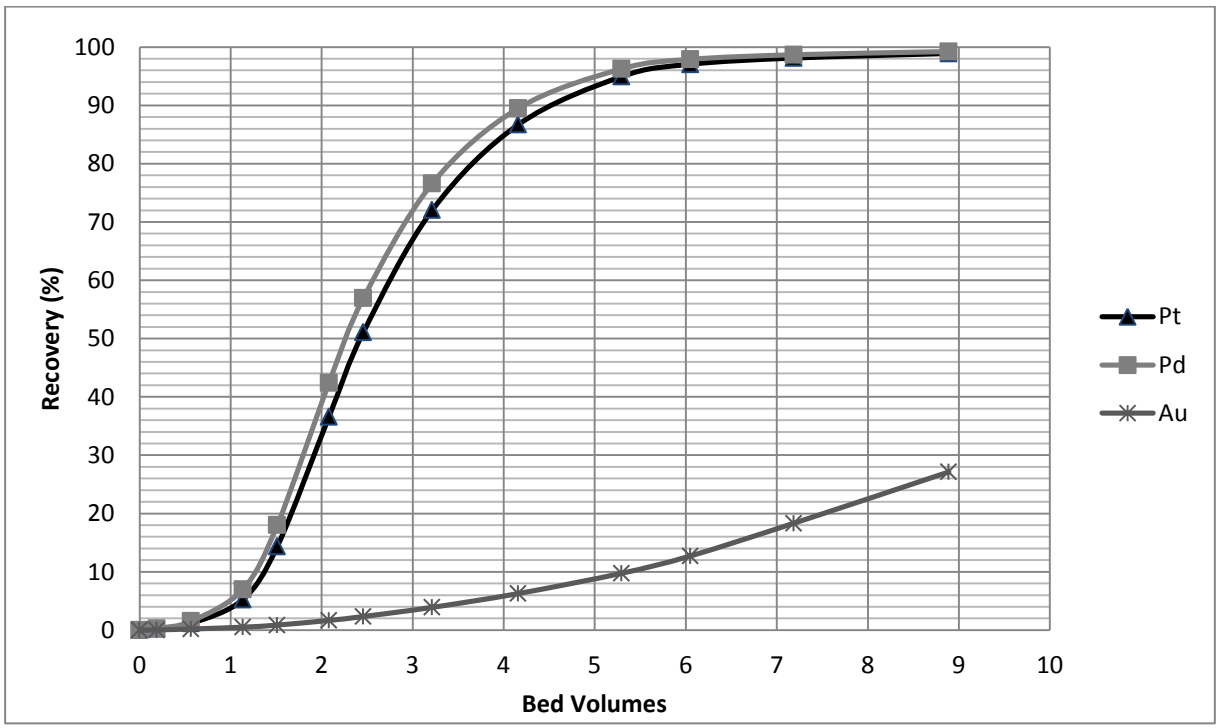
Date	25-Jan	
Pre-treatment step		**wt %**
NaOH (g)	0.44	1.1
NaCN (g)	1.6	4
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	11.14
Flow rate (BV/hr)	2.1

	mg/L	Au	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	AC1	0.79	21520.0	0.06	0.01					
water	AC2	0.08	4.28	0.00	0.00					
	AC3	1.47	5001.00	10.69	9.28	5.9	10:58	11:07	9	2.81
	AC4	1.54	7815.00	11.34	9.81	5.9	11:07	11:18	11	2.30
	AC5	2.55	4281.00	54.09	46.18	5.4	11:18	11:29	11	2.10
	AC6	4.50	1637.00	143.60	140.70	5.6	11:29	11:42	13	1.85
	AC7	5.98	940.00	147.50	163.40	5	11:42	11:56	14	1.53
	AC8	7.21	676.60	112.70	133.90	5	11:56	12:07	11	1.95
	AC9	8.19	474.40	63.58	80.80	5	12:13	12:25	12	1.79
	AC10	10.45	336.30	28.80	39.54	5.1	12:38	12:51	13	1.68
	AC11	12.31	242.40	11.52	16.78	5.5	13:06	13:18	12	1.96
	AC12	16.90	154.00	3.11	4.77	5.4	13:31	13:39	8	2.89
	AC13	19.77	124.30	1.55	2.53	5.7		14:12		
	AC14	18.63	105.00	0.64	1.04	6.5	14:42	14:54	12	2.32
bulk	AC15	14.60	160.90	8.51	11.25	6.5				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.01	**0.00**	0.01	0.00	0.00	0.00
2.65	0.19	0.06	0.30	0.05	0.23	0.01	0.04
7.94	0.57	0.26	1.53	0.22	1.16	0.02	0.19
15.89	1.13	0.52	7.01	0.49	5.25	0.02	0.50
21.18	1.51	1.16	18.04	1.21	14.37	0.04	0.86
29.13	2.08	0.69	42.42	0.79	36.61	0.03	1.66
34.42	2.46	0.93	56.94	1.14	51.10	0.08	2.33
45.01	3.22	0.61	76.62	0.80	72.04	0.12	3.90
58.25	4.16	0.32	89.51	0.45	86.71	0.18	6.27
74.14	5.30	0.08	96.26	0.11	94.95	0.15	9.75
84.73	6.05	0.04	97.90	0.06	97.05	0.29	12.73
100.62	7.19	0.03	98.68	0.04	98.12	0.46	18.33
124.45	8.89	0.04	99.23	0.06	98.90		27.13
Sum		**4.74**		**5.43**		**1.41**	



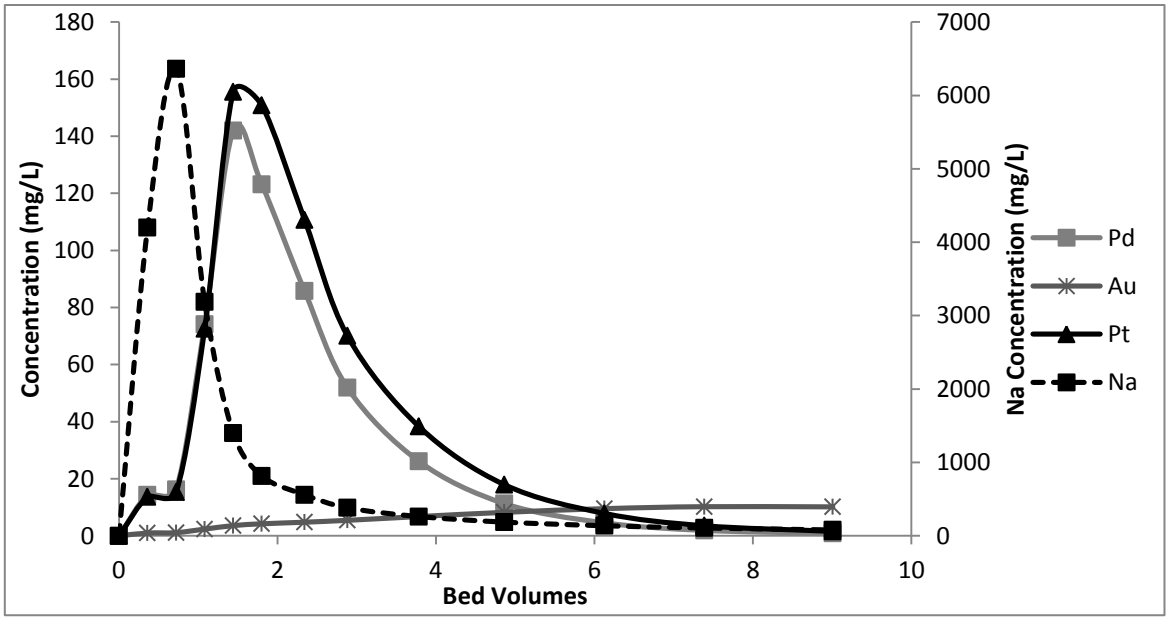
Elution experiment AD

Loading experiment D

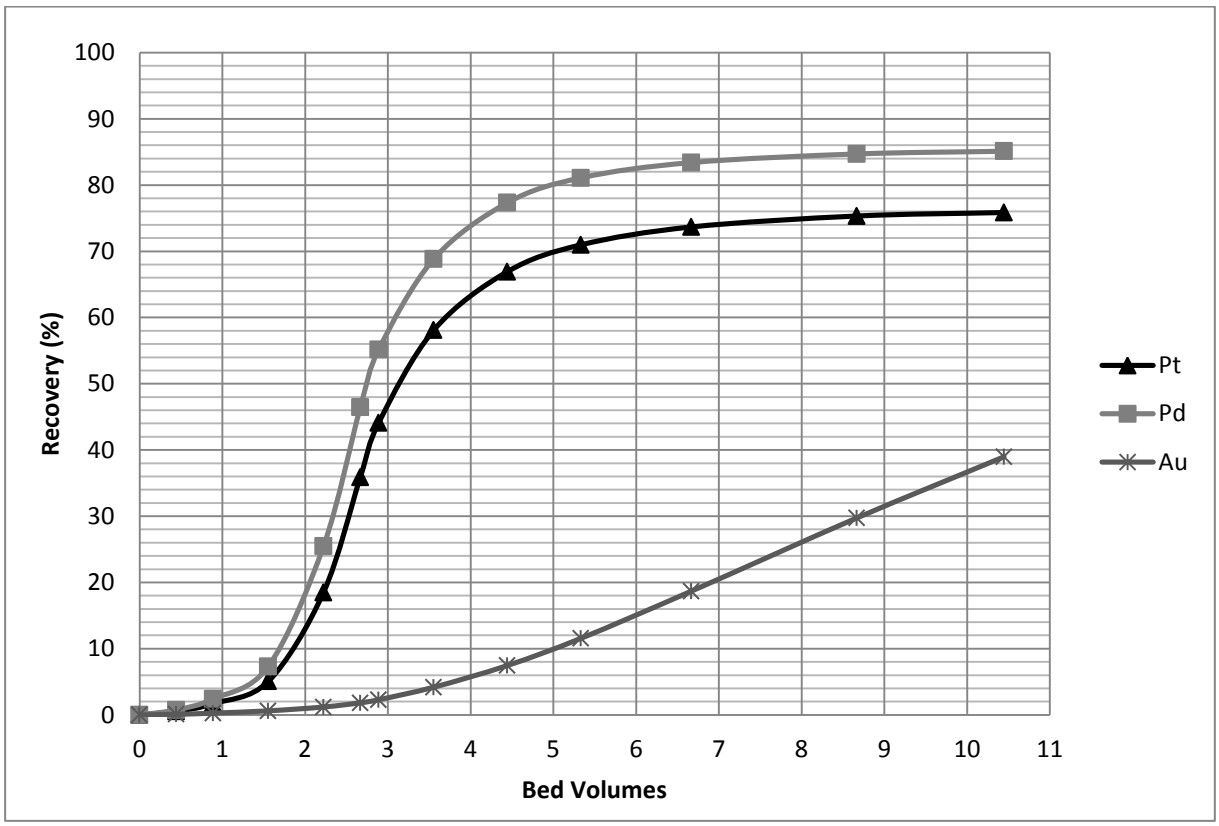
Date	25-Jan	
Pre-treatment step		**wt %**
NaOH (g)	0.66	1.65
NaCN (g)	1.6	4
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	11.14
Flow rate (BV/hr)	2.7

	mg/L	**Au**	**Cu**	**Na**	**Pd**	**Pt**	**Sample Volume**	**Sample Start**	**Sample stop**	**Time (min)**	**Flow rate (BV/hr)**
pre-treatment	AA1	nd	0.51	17270.00	nd	nd					
water	AA2	nd	0.01	1.65	nd	nd					
	AA3	0.96	1.10	4199.00	14.27	13.66	5.7	09:57	10:07	10	2.44
	AA4	1.11	1.56	6360.00	16.20	15.33	5.7	10:07	10:17	10	2.44
	AA5	2.35	1.31	3187.00	74.14	72.51	5.4	10:17	10:26	9	2.57
	AA6	3.57	0.63	1399.00	141.90	155.50	5.1	10:26	10:36	10	2.19
	AA7	4.21	0.25	815.80	123.10	150.80	6.2	10:36	10:48	12	2.21
	AA8	4.76	0.12	559.10	85.75	110.70	5.5	10:48	10:59	11	2.14
	AA9	5.43	0.06	381.30	51.86	70.04	6.1	11:04	11:17	13	2.01
	AA10	6.74	0.03	262.20	26.13	38.33	5.1	11:28	11:39	11	1.99
	AA11	8.22	0.02	186.30	11.27	17.90	6	11:55	12:08	13	1.98
	AA12	9.51	0.01	137.00	4.55	7.84	5.4	12:31	12:43	12	1.93
	AA13	10.20	0.01	106.40	1.90	3.52	5.3	13:07	13:19	12	1.89
	AA14	10.14	0.00	79.88	0.81	1.56	6.5	13:50	14:03	13	2.14
bulk	AA15	8.74	0.03	139.70	9.17	14.33	8.6				



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)	Na (mg)
0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.00	17.10
5.78	0.44	0.07	0.75	0.06	0.54	0.01	0.09	41.75
11.56	0.89	0.21	2.41	0.17	1.70	0.02	0.27	64.29
20.22	1.56	0.76	7.33	0.68	5.07	0.03	0.61	37.53
28.89	2.22	0.88	25.48	0.89	18.49	0.03	1.19	10.11
34.67	2.67	0.37	46.44	0.42	35.90	0.02	1.83	2.56
37.56	2.89	0.58	55.17	0.71	44.11	0.10	2.29	4.35
46.23	3.56	0.36	68.86	0.45	58.12	0.17	4.19	3.77
57.78	4.44	0.16	77.33	0.21	66.92	0.21	7.46	2.80
69.34	5.33	0.10	81.09	0.14	70.97	0.37	11.57	3.18
86.67	6.67	0.05	83.40	0.08	73.67	0.57	18.69	3.74
112.68	8.67	0.02	84.70	0.03	75.33	0.48	29.74	2.80
135.79	10.45		85.11		75.85		38.98	
Sum		**3.58**		**3.87**		**2.03**		**193.97**



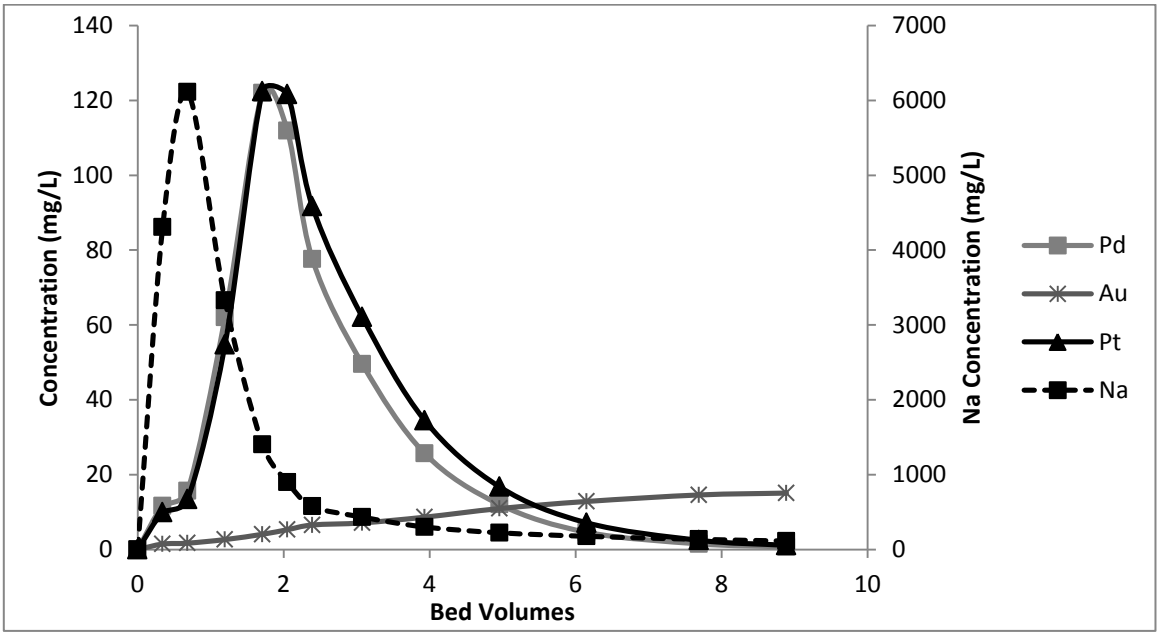
Elution experiment AE

Loading experiment D

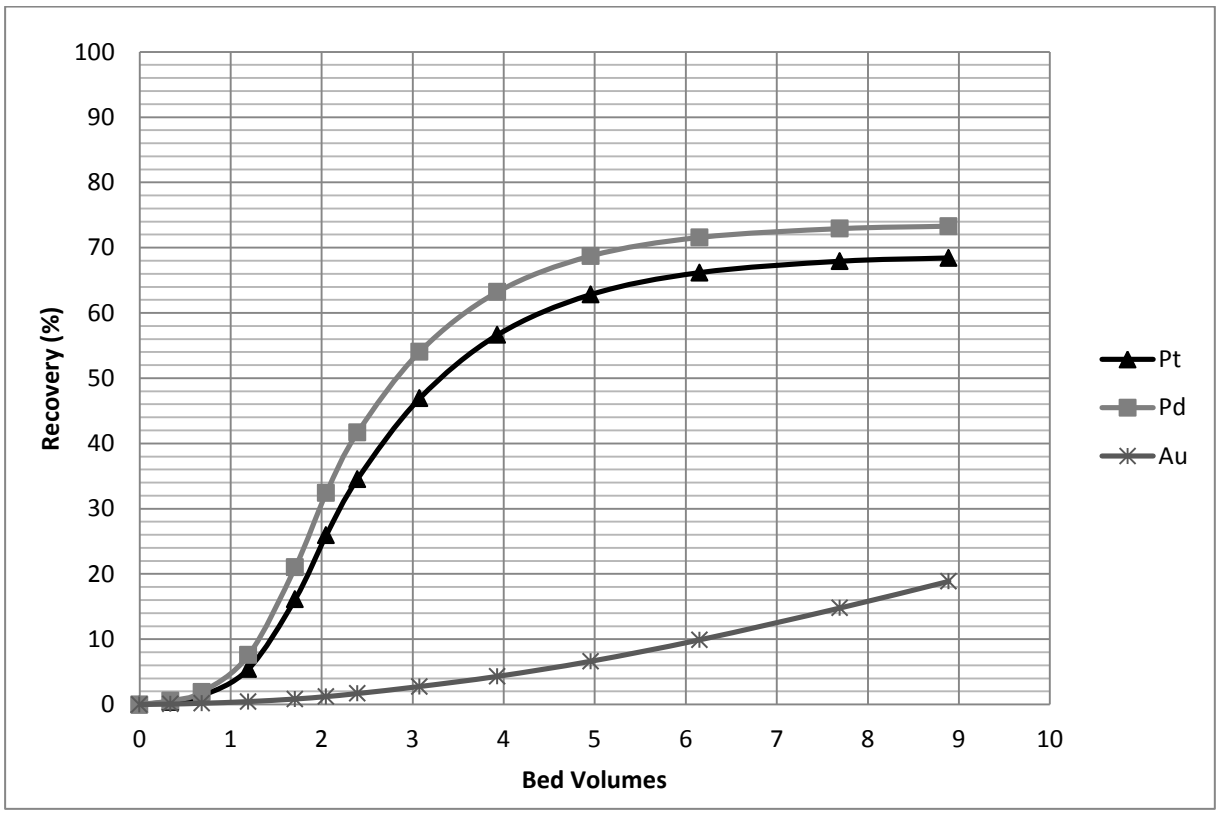
Pre-treatment step		wt %
NaOH (g)	0.66	1.65
NaCN (g)	1.2	3
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	12
pH after	11.14
Flow rate (BV/hr)	2.1

	mg/L	Au	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
pre-treatment	AE1	nd	20350.0	nd	< 0.05					
water	AE2	nd	3.63	nd	< 0.05					
	AE3	1.46	4306.00	11.63	9.91	5.50	09:23	09:36	13	2.12
	AE4	1.70	6111.00	15.65	13.42	5.30	09:36	09:47	11	2.41
	AE5	2.66	3326.00	62.04	54.78	5.10	09:47	10:00	13	1.96
	AE6	4.07	1404.00	122.00	122.40	5.40	10:00	10:15	15	1.80
	AE7	5.30	900.90	111.90	121.60	5.40	10:15	10:27	12	2.25
	AE8	6.55	579.00	77.60	91.70	5.40	10:27	10:38	11	2.45
	AE9	7.11	433.10	49.58	62.13	5.20	10:44	10:56	12	2.17
	AE10	8.64	300.80	25.68	34.52	5.50	11:06	11:20	14	1.96
	AE11	10.94	223.80	12.05	16.76	5.50	11:35	11:49	14	1.96
	AE12	12.84	176.30	4.60	7.13	6.00	12:10	12:26	16	1.88
	AE13	14.58	135.80	1.51	2.47	6.00	12:56	13:12	16	1.88
	AE14	15.08	113.80	0.68	1.13	5.70	13:34	13:50	16	1.78
bulk	AE15	11.53	169.50	8.95	11.35					



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00
4.10	0.34	0.06	0.57	0.05	0.40	0.01	0.06
8.21	0.68	0.24	1.90	0.21	1.34	0.01	0.18
14.36	1.20	0.57	7.57	0.55	5.45	0.02	0.44
20.51	1.71	0.48	21.03	0.50	16.14	0.02	0.84
24.62	2.05	0.39	32.42	0.44	25.96	0.02	1.21
28.72	2.39	0.52	41.66	0.63	34.54	0.06	1.68
36.93	3.08	0.39	54.05	0.50	46.91	0.08	2.75
47.18	3.93	0.23	63.22	0.32	56.63	0.12	4.31
59.49	4.96	0.12	68.74	0.17	62.82	0.17	6.62
73.85	6.15	0.06	71.58	0.09	66.18	0.25	9.91
92.31	7.69	0.02	72.92	0.03	67.92	0.21	14.78
106.67	8.89		73.29		68.42		18.87
Sum		**3.09**		**3.49**		**0.98**	

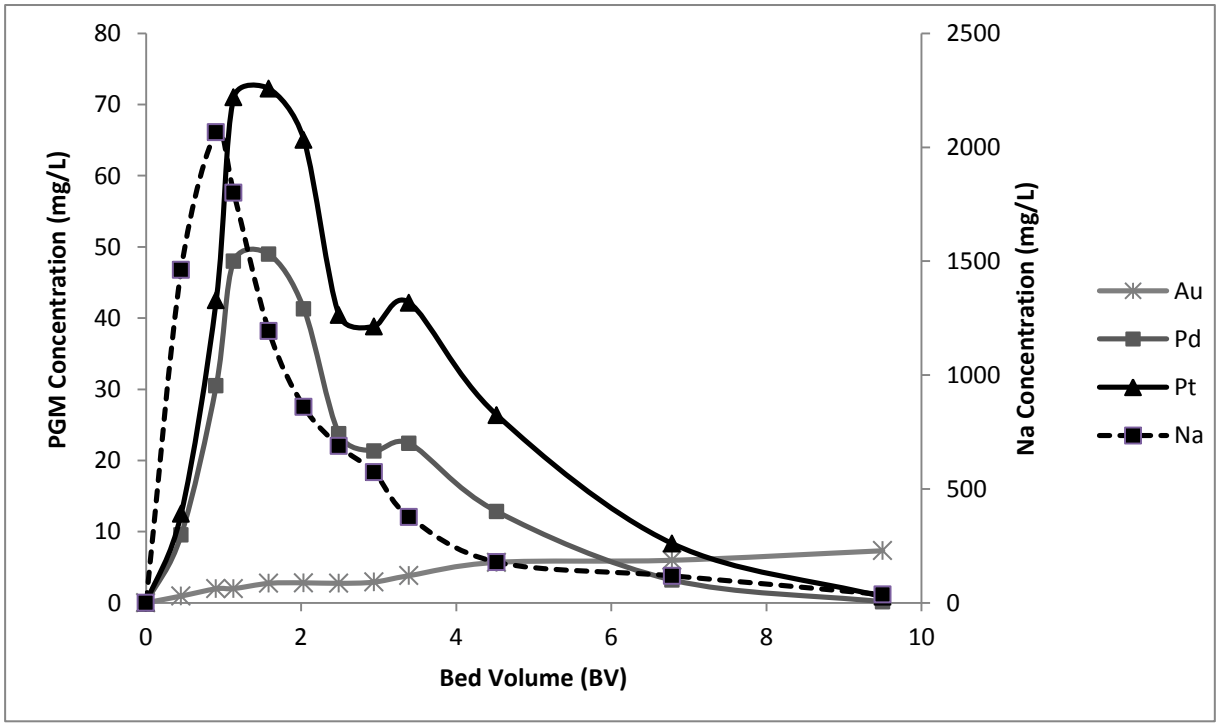


Elution experiment AE

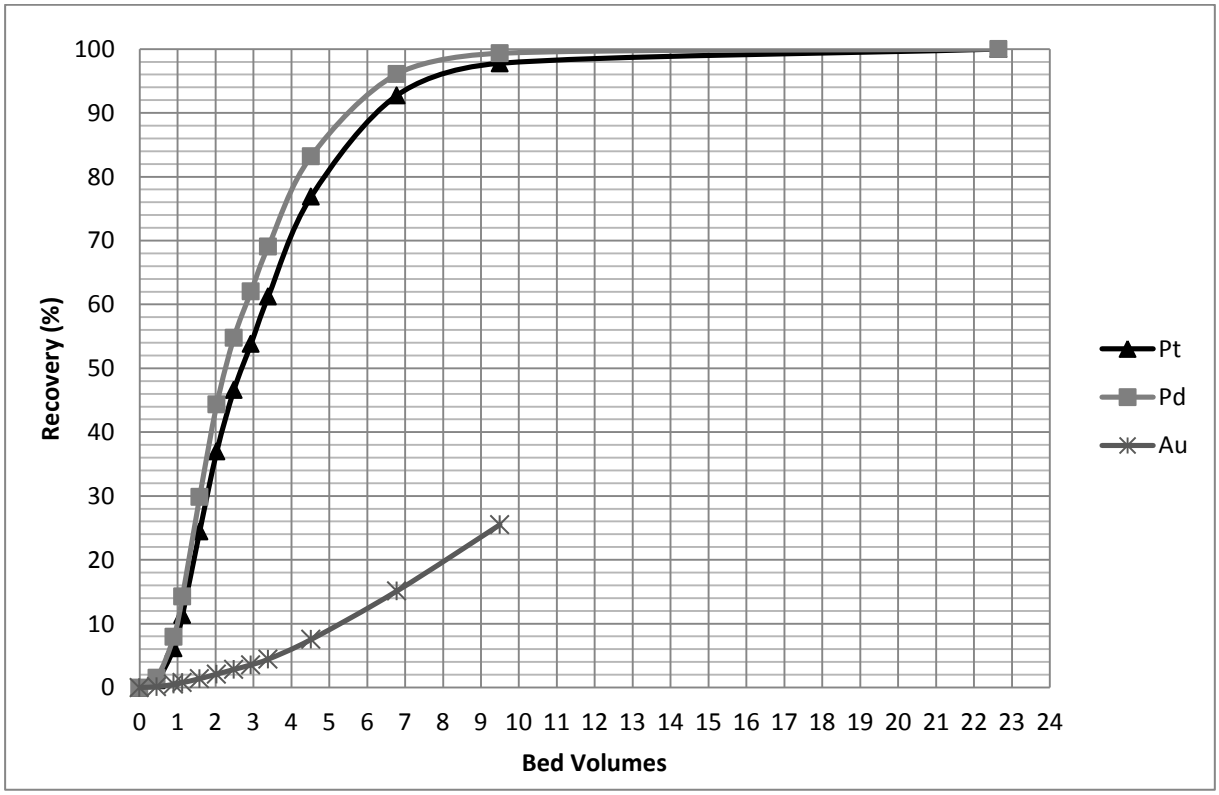
Date	25-Jul 14
Pre-treatment step	
NaOH (%)	0.6
NaCN (%)	2
Volume (ml)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (ml)	14
pH after	
Flow rate (BV/hr)	2.7

ppm	Au	Na	Pd	Pt	Sample Volume (ml)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
AE1	0.948	1461.925	9.530	12.495	6	14:33	14:39	6	4.29
AE2	1.972	2066.478	30.510	42.503	6	14:39	14:47	8	3.21
AE3	0.217	-36.802	-0.780	-0.083	6	14:47	14:56	9	2.86
AE4	2.735	1192.822	48.970	72.248	6	14:56	15:06	10	2.57
AE5	2.809	860.344	41.278	65.026	5.3	15:06	15:15	9	2.52
AE6	2.736	688.196	23.731	40.425	5.5	15:15	15:25	10	2.36
AE7	2.906	573.346	21.341	38.830	5.5	15:25	15:35	10	2.36
AE8	3.815	377.411	22.392	42.166	6	15:35	15:46	11	2.34
AE9	5.684	178.227	12.823	26.364	6	15:59	16:10	11	2.34
AE10	5.973	118.368	3.208	8.321	5.9	16:50	17:01	11	2.30
AE11	7.315	36.355	0.143	0.841		17:50	18:00		



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.03	0.00	0.04	0.00	0.00	0.00
6.33	0.45	0.13	1.53	0.17	1.14	0.01	0.12
12.67	0.90	0.12	7.97	0.18	6.17	0.01	0.50
15.83	1.13	0.31	14.27	0.45	11.35	0.01	0.76
22.16	1.58	0.29	29.86	0.43	24.44	0.02	1.38
28.50	2.04	0.21	44.36	0.33	36.98	0.02	2.10
34.83	2.49	0.14	54.81	0.25	46.61	0.02	2.82
41.16	2.94	0.14	62.05	0.26	53.85	0.02	3.56
47.50	3.39	0.28	69.08	0.54	61.25	0.08	4.43
63.33	4.52	0.25	83.22	0.55	76.90	0.18	7.53
94.99	6.79	0.06	96.10	0.17	92.75	0.25	15.12
132.99	9.50	0.01	99.33	0.08	97.77		25.50
317.10	22.65		100.00		100.00		
		1.97		**3.47**		**0.62**	

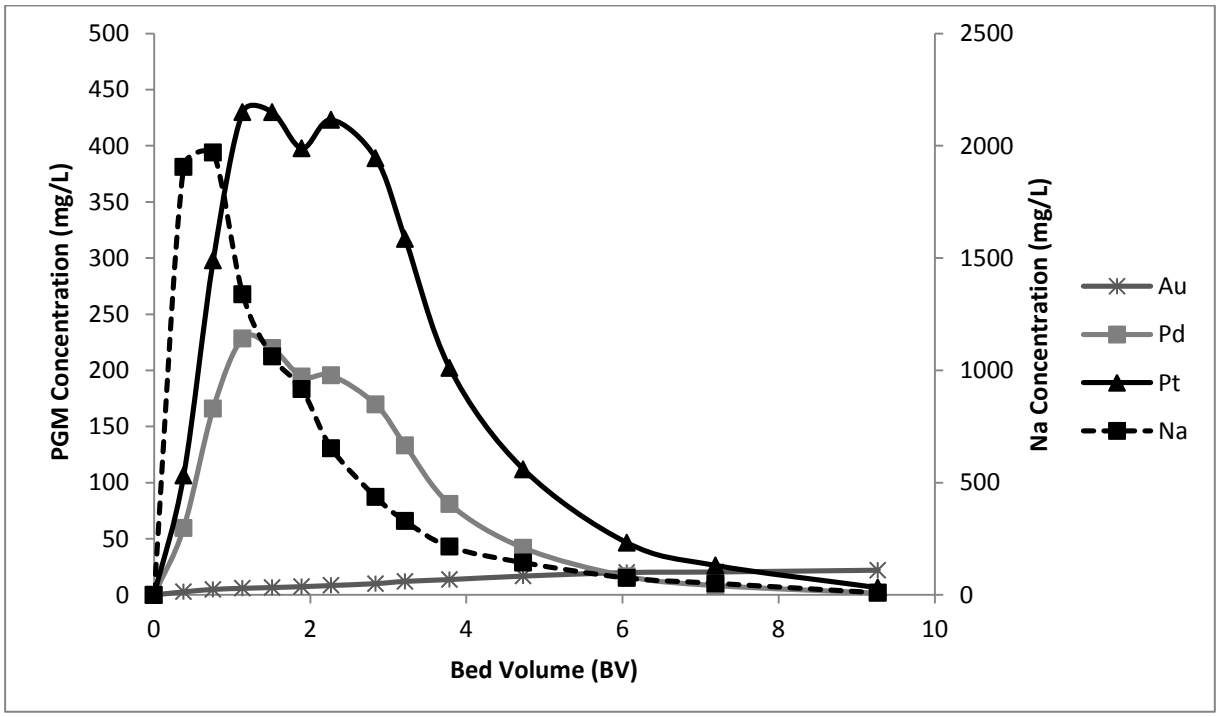


Elution experiment AF

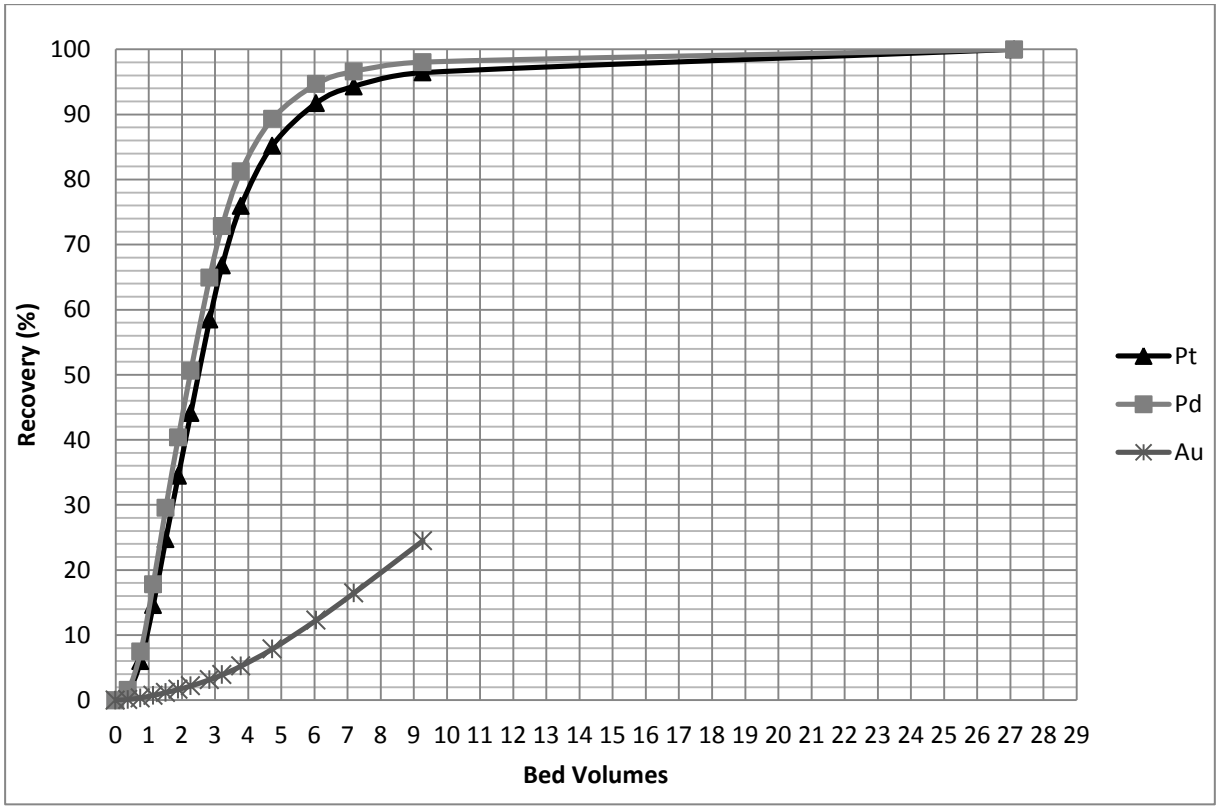
Date	25-Jul 14
Pre-treatment step	
NaOH (%)	0.6
NaCN (%)	2
Volume (ml)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (ml)	14
pH after	
Flow rate (BV/hr)	2.3

ppm	Au	Na	Pd	Pt	Sample Volume (ml)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
AF1	2.75	1905.21	59.61	106.27	5.2	15:03	15:08	5	4.46
AF2	4.96	1970.18	165.99	297.88	5.4	15:08	15:18	10	2.31
AF3	5.88	1338.36	228.42	429.93	5.5	15:18	15:29	11	2.14
AF4	6.59	1061.55	219.69	429.98	5.5	15:29	15:41	12	1.96
AF5	7.36	916.65	194.30	397.78	5	15:41	15:52	11	1.95
AF6	8.40	653.17	195.42	423.05	5.4	15:52	16:03	11	2.10
AF7	10.08	435.92	169.67	388.97	5.4	16:03	16:14	11	2.10
AF8	12.09	328.64	133.02	316.87	5.3	16:14	16:25	11	2.06
AF9	13.69	214.48	80.90	202.17	5	16:31	16:42	11	1.95
AF10	16.80	143.76	41.82	111.86	6.8	16:54	17:07	13	2.24
AF11	19.93	75.34	16.55	46.49	5.7	17:30	17:42	12	2.04
AF12	20.46	51.73	8.34	26.25	5.4	17:57	18:09	12	1.93
AF13	22.02	9.52	1.59	6.43	5.1	18:56	19:06	10	2.19



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.16	0.00	0.28	0.00	0.01	0.00
5.30	0.38	0.60	1.56	1.07	1.25	0.02	0.09
10.60	0.76	1.05	7.47	1.93	6.01	0.03	0.36
15.90	1.14	1.19	17.80	2.28	14.58	0.03	0.73
21.20	1.51	1.10	29.54	2.19	24.71	0.04	1.16
26.50	1.89	1.03	40.38	2.17	34.46	0.04	1.64
31.80	2.27	1.45	50.59	3.23	44.13	0.07	2.19
39.74	2.84	0.80	64.94	1.87	58.48	0.06	3.14
45.04	3.22	0.85	72.86	2.06	66.79	0.10	3.90
52.99	3.79	0.81	81.27	2.08	75.96	0.20	5.24
66.24	4.73	0.54	89.31	1.47	85.21	0.34	7.86
84.79	6.06	0.20	94.66	0.58	91.74	0.32	12.28
100.69	7.19	0.14	96.61	0.48	94.31	0.62	16.46
129.83	9.27	0.20	98.04	0.80	96.43		24.50
379.74	27.12		100.00		100.00		
		10.12		**22.50**		**1.89**	

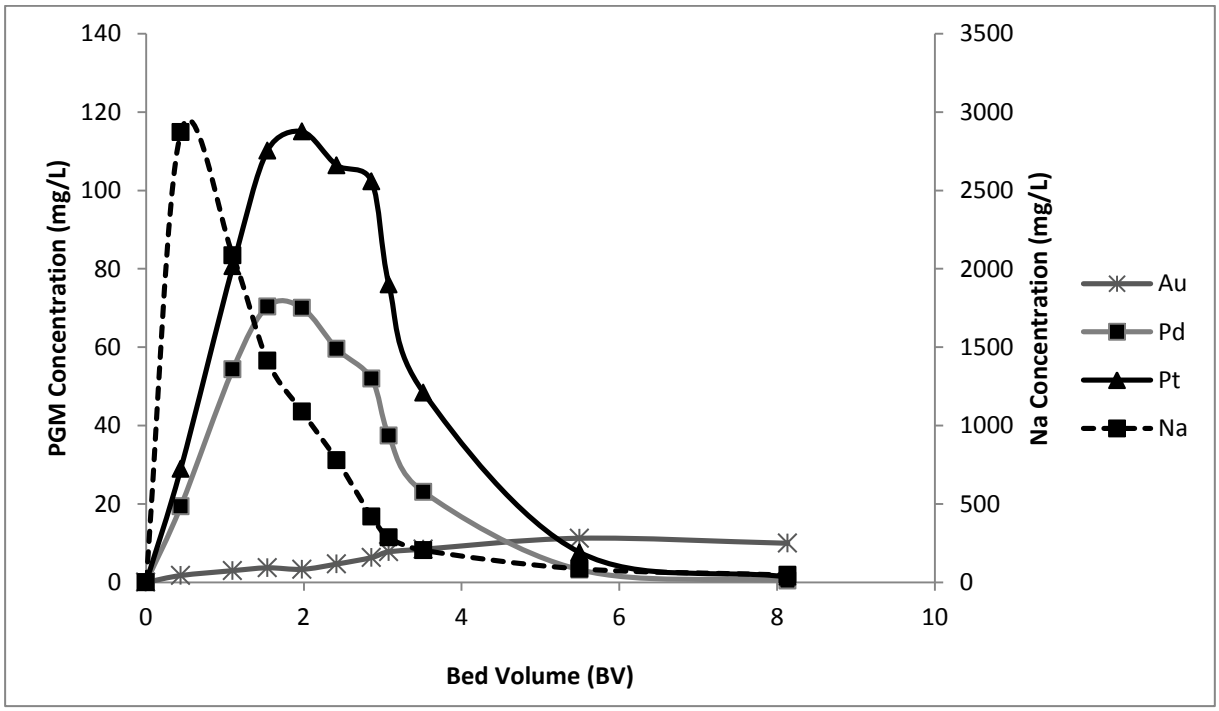


Elution experiment AG

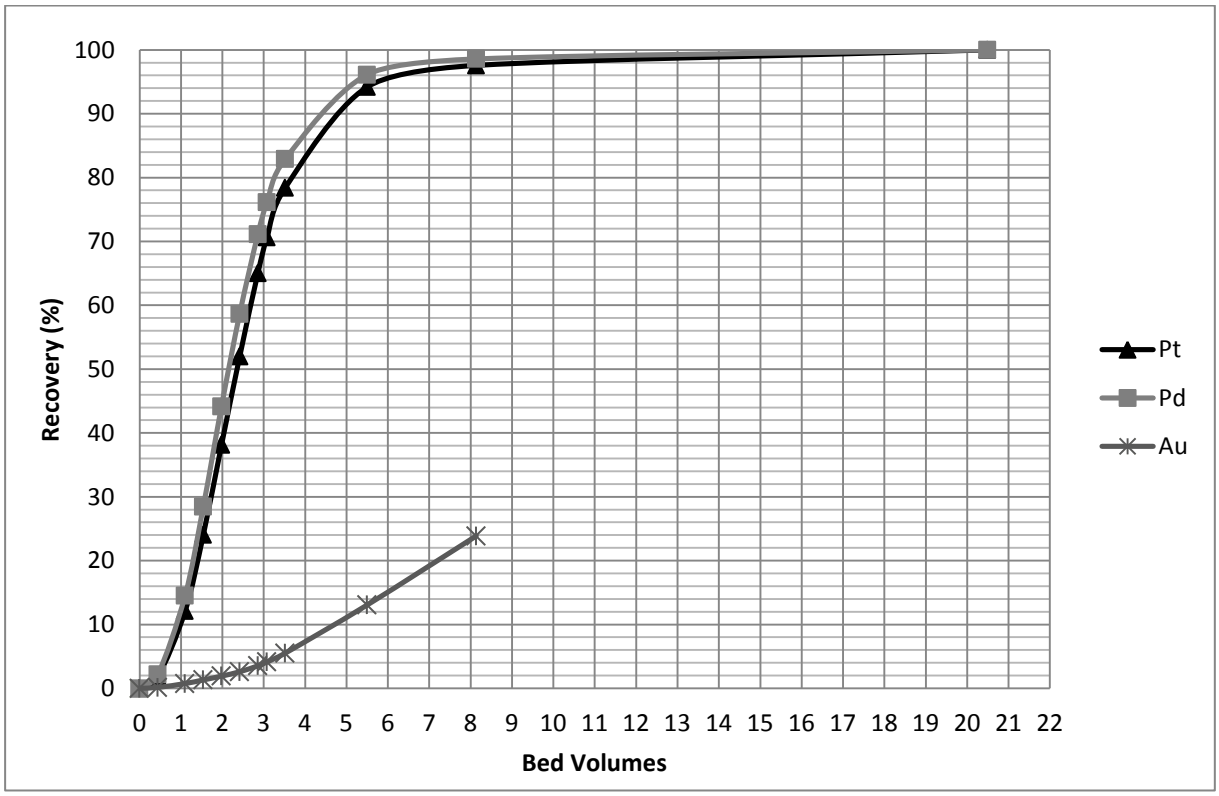
Date	25-Jul 14
Pre-treatment step	
NaOH (%)	0.6
NaCN (%)	2
Volume (ml)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (ml)	14
pH after	
Flow rate (BV/hr)	2.6

ppm	Au	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
AG1	1.74	2870.82	19.40	28.96	5.5	11:26	11:37	11	2.14
AG2	2.98	2084.90	54.31	80.62	5.2	11:37	11:48	11	2.03
AG3	3.71	1414.10	70.36	110.17	5.4	11:48	11:59	11	2.10
AG4	3.33	1089.40	51.68	85.04	5.3	11:59	12:09	10	2.27
AG5	4.67	778.65	59.58	106.40	6	12:09	12:19	10	2.57
AG6	6.32	419.91	51.94	102.33	6.5	12:19	12:29	10	2.79
AG7	7.82	285.48	37.43	75.99	6.5	12:29	12:37	8	3.48
AG8	8.45	204.29	23.05	48.41	5	12:37	12:46	9	2.38
AG9	11.25	85.92	3.22	7.65	6.5	13:25	13:32	7	3.98
AG10	9.97	46.95	0.45	1.38	6	14:22			



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.06	0.00	0.09	0.00	0.01	0.00
6.16	0.44	0.34	2.17	0.51	1.81	0.02	0.15
15.39	1.10	0.38	14.53	0.59	12.10	0.02	0.75
21.55	1.54	0.43	28.47	0.69	24.03	0.02	1.32
27.70	1.98	0.40	44.17	0.68	38.12	0.02	1.92
33.86	2.42	0.34	58.66	0.64	51.97	0.03	2.60
40.01	2.86	0.14	71.13	0.27	65.03	0.02	3.53
43.09	3.08	0.19	76.13	0.38	70.61	0.05	4.13
49.25	3.52	0.36	82.89	0.78	78.39	0.27	5.51
76.95	5.50	0.07	96.11	0.17	94.18	0.39	13.05
113.88	8.13	0.04	98.58	0.12	97.57		23.87
286.89	20.49		100.00		100.00		
		2.75		**4.92**		**0.86**	

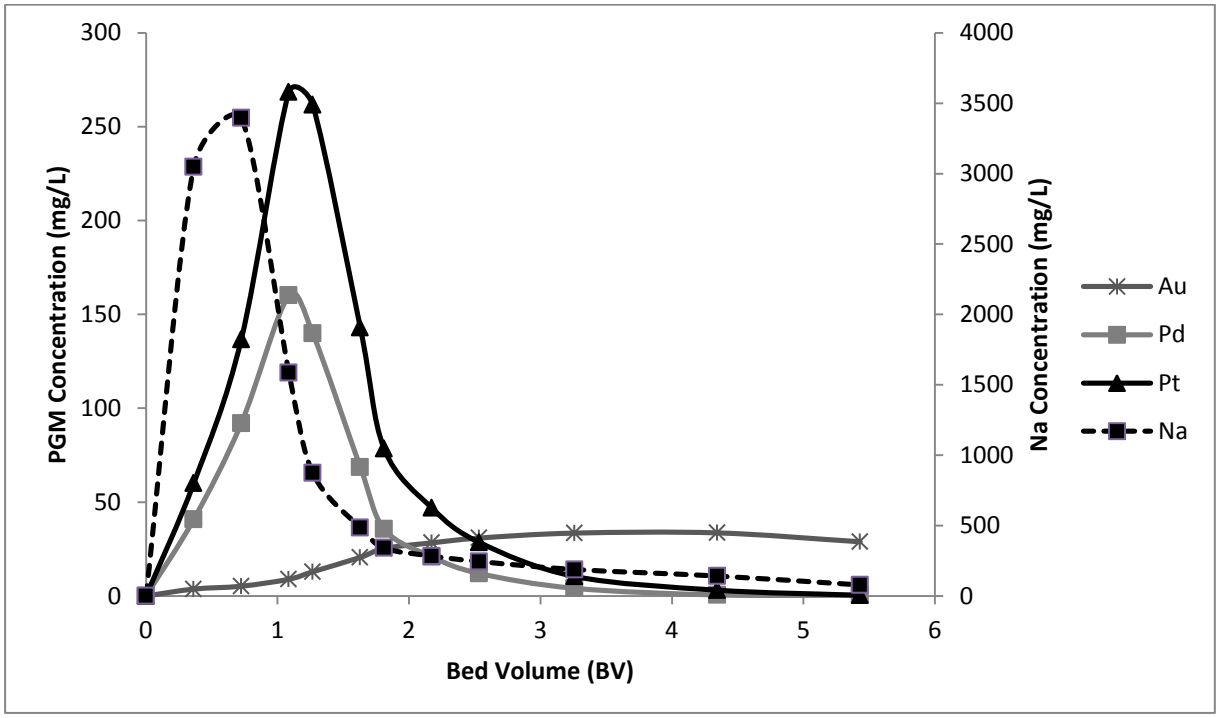


Elution experiment AH

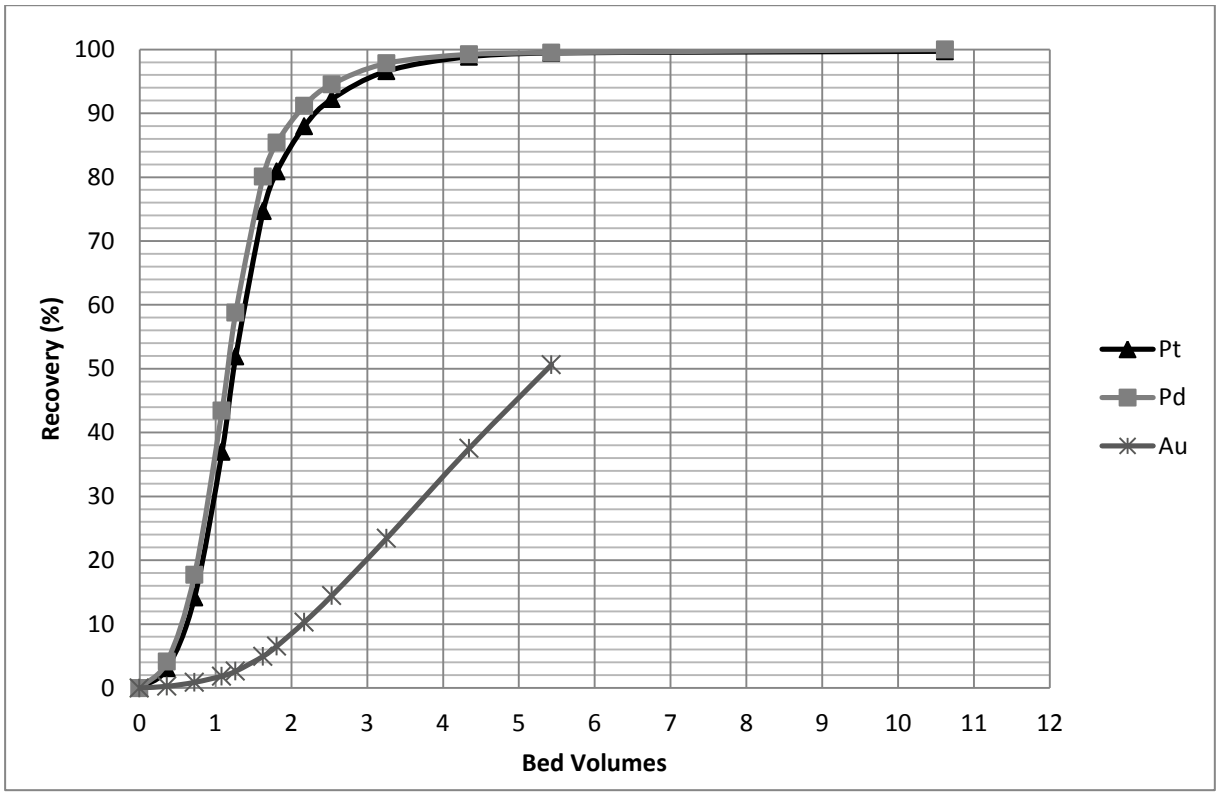
Date	25-Jul 14
Pre-treatment step	
NaOH (%)	0.6
NaCN (%)	2
Volume (ml)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	95
Bed Volume (ml)	14
pH after	
Flow rate (BV/hr)	2.2

ppm	Au	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
AH1	3.64	3047.13	40.76	59.99	4	16:31	16:43	12	1.43
AH2	5.18	3395.58	91.93	136.64	4	16:43	16:49	6	2.86
AH3	8.90	1586.45	160.23	268.44	4.1	16:49	17:00	11	1.60
AH4	12.88	873.75	139.95	261.63	3.9	17:00	17:07	7	2.39
AH5	20.55	484.46	68.61	142.92	4.5	17:07	17:14	7	2.76
AH6	25.31	340.66	35.65	78.47	4.5	17:14	17:22	8	2.41
AH7	28.28	283.47	20.88	46.92	4.1	17:22	17:30	8	2.20
AH8	30.83	244.46	11.97	28.51	4.2	17:30	17:38	8	2.25
AH9	33.47	187.79	4.05	10.39	4.6	17:48	17:58	10	1.97
AH10	33.58	141.25	0.53	3.06	4.8	18:20	18:31	11	1.87
AH11	28.86	77.97	0.34	0.33	7.1	18:50			



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.10	0.00	0.15	0.00	0.01	0.00
5.07	0.36	0.34	4.16	0.50	3.09	0.02	0.25
10.14	0.72	0.64	17.72	1.03	14.16	0.04	0.87
15.21	1.09	0.38	43.47	0.67	36.97	0.03	1.86
17.74	1.27	0.53	58.80	1.03	51.90	0.08	2.62
22.81	1.63	0.13	80.11	0.28	74.68	0.06	4.96
25.35	1.81	0.14	85.43	0.32	80.91	0.14	6.56
30.41	2.17	0.08	91.20	0.19	87.98	0.15	10.31
35.48	2.53	0.08	94.56	0.20	92.22	0.33	14.45
45.62	3.26	0.03	97.83	0.10	96.60	0.51	23.45
60.83	4.34	0.01	99.24	0.03	98.88	0.47	37.52
76.04	5.43	0.01	99.50	0.01	99.45		50.63
148.68	10.62		100.00		99.71		
		2.48		**4.50**		**1.83**	

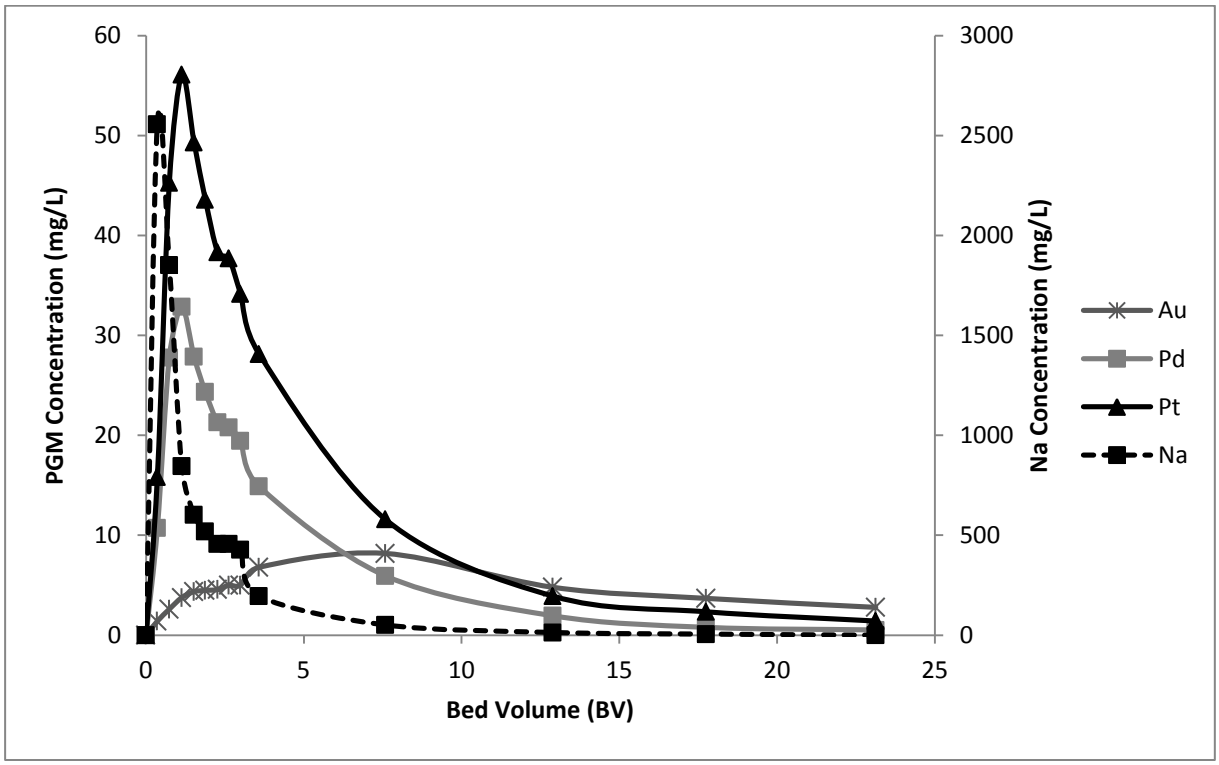


Elution experiment AI

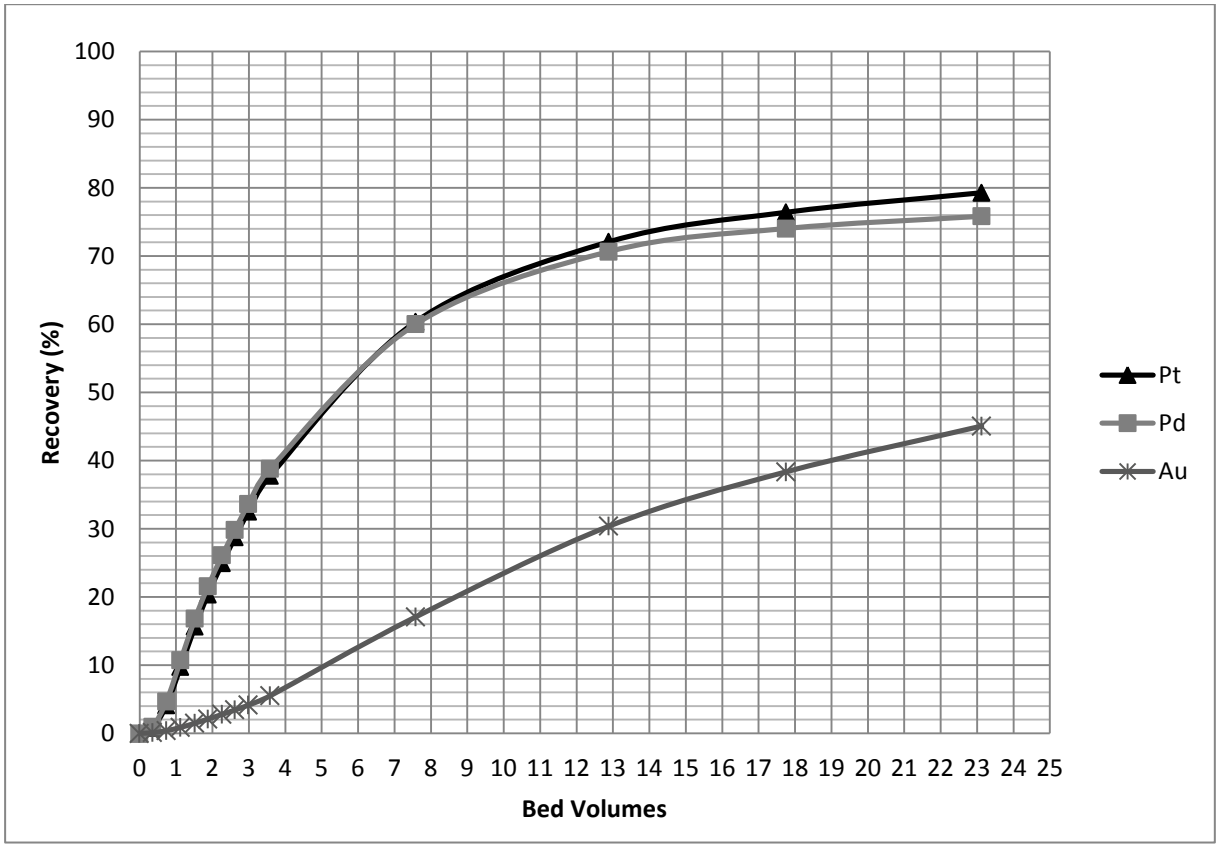
Date	25-Jul 14
Pre-treatment step	
NaOH (%)	0.6
NaCN (%)	2
Volume (ml)	40
Stirred (min)	30
pH	
Activated Carbon (wet g)	12

Elution	
Temperature (°C)	80
Bed Volume (ml)	14
pH after	
Flow rate (BV/hr)	27.0

ppm	Au	Na	Pd	Pt	Sample Volume	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
AI1	1.40	2556.81	10.73	15.84	5				27.00
AI2	2.60	1851.97	27.78	45.27	5.3				27.00
AI3	3.75	845.40	32.87	56.09	5.5				27.00
AI4	4.36	602.32	27.86	49.30	5.5				27.00
AI5	4.47	519.20	24.34	43.57	5				27.00
AI6	4.57	457.09	21.31	38.30	5.5				27.00
AI7	4.99	456.86	20.80	37.70	4.9				27.00
AI8	5.01	427.95	19.45	34.17	5.2				27.00
AI9	6.80	196.28	14.89	28.14	5.1	13:46			27.00
AI10	8.18	51.32	5.94	11.59	5.6	13:55			27.00
AI11	4.80	13.65	1.95	3.92	5	14:06			27.00
AI12	3.68	5.55	0.79	2.34	5.1	14:16			27.00
AI13	2.78	-0.20	0.53	1.42	5.9	14:27			27.00



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.03	**0.00**	0.04	0.00	0.00	0.00
5.00	0.36	0.10	0.97	0.16	0.80	0.01	0.10
10.30	0.74	0.17	4.68	0.28	4.10	0.02	0.39
15.80	1.13	0.17	10.74	0.29	9.76	0.02	0.87
21.30	1.52	0.13	16.81	0.23	15.65	0.02	1.49
26.30	1.88	0.13	21.55	0.23	20.37	0.02	2.10
31.80	2.27	0.10	26.11	0.19	24.95	0.02	2.79
36.70	2.62	0.10	29.86	0.19	28.74	0.03	3.43
41.90	2.99	0.14	33.66	0.26	32.53	0.05	4.15
50.15	3.58	0.58	38.81	1.11	37.76	0.42	5.50
106.15	7.58	0.29	60.01	0.58	60.38	0.48	17.07
180.45	12.89	0.09	70.66	0.21	72.09	0.29	30.38
248.55	17.75	0.05	74.04	0.14	76.42	0.24	38.35
323.75	23.13		75.83		79.29		45.06
		2.04		**3.76**		**1.39**	



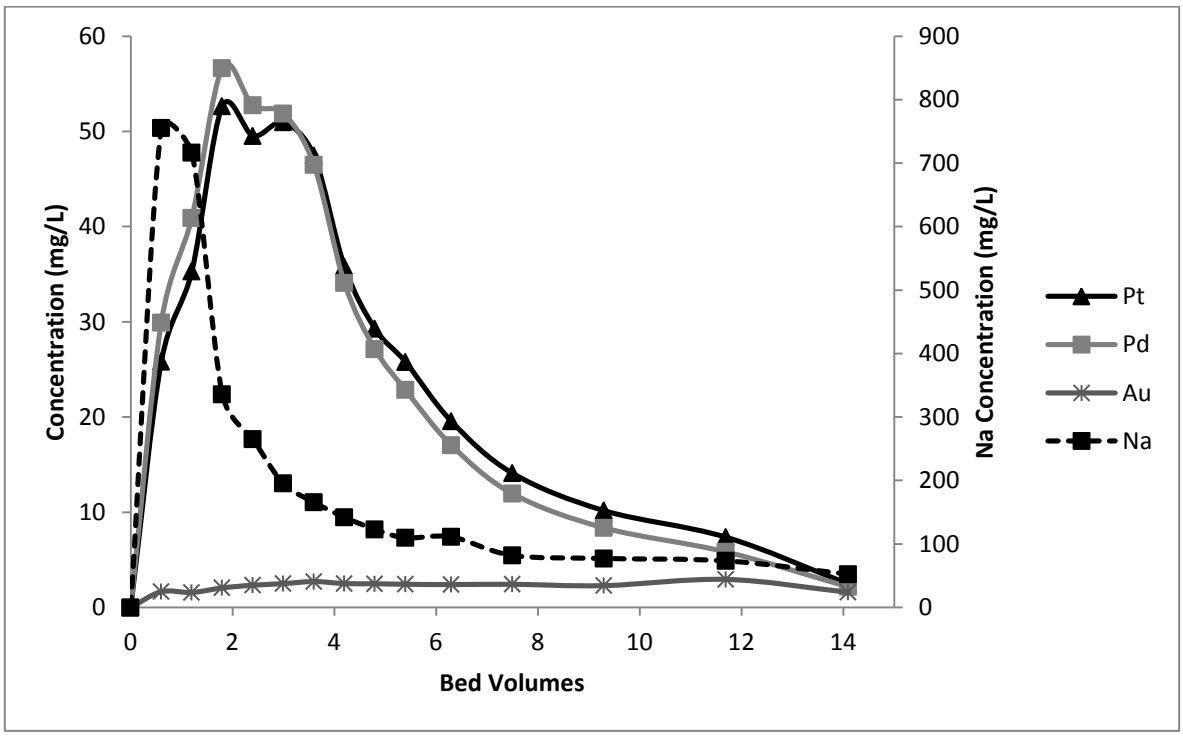
Elution experiment Repeat 1

Loading experiment I

Date		
Pre-treatment step		**wt %**
NaOH (g)	0.22	0.55
NaCN (g)	0	0
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

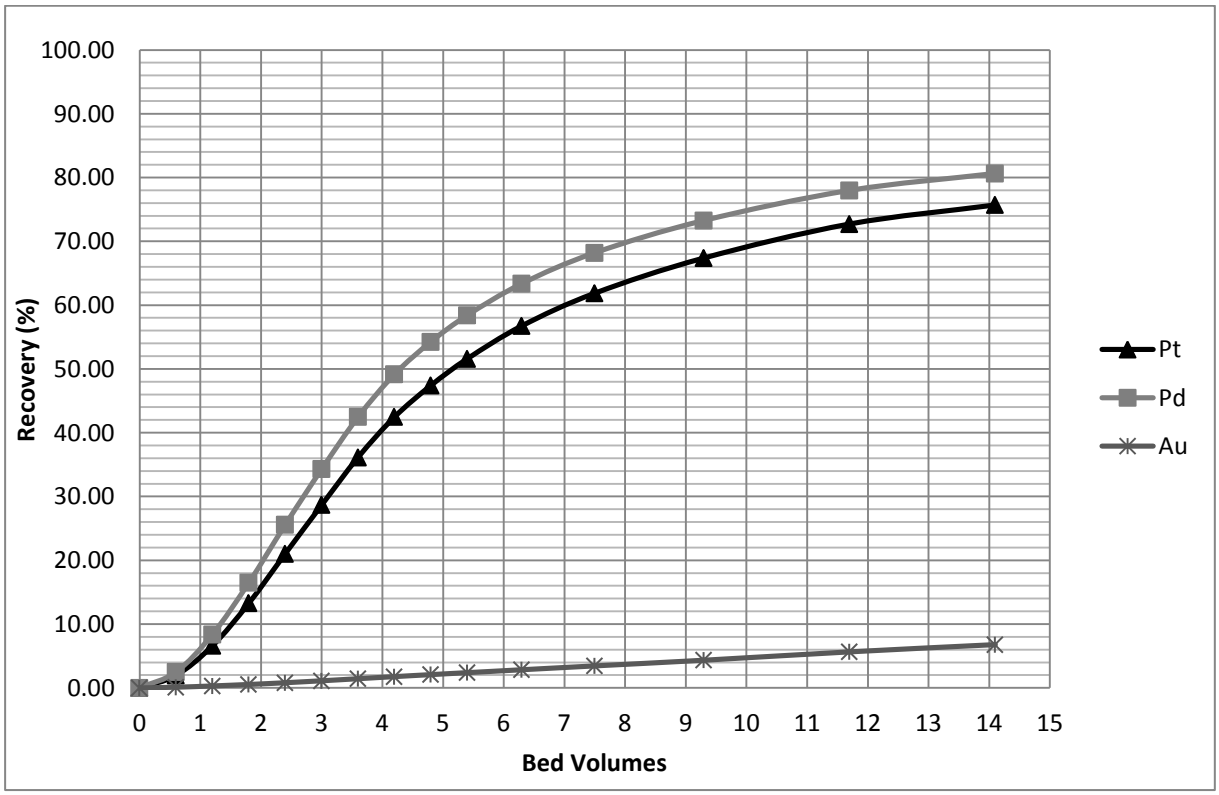
Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	
Flow rate (BV/hr)	3.6

	mg/L	**Au**	**Na**	**Pd**	**Pt**	**Sample Time**
pre-treatment		nd	2527.50	0.23	nd	The times for the first two repeat runs were every 10min for the first 9 samples and then in increments of 5, 10, 20, 30 and 40 min
water		0.06	10.54	0.02	0.02	
	R1:1	1.65	755.25	29.93	25.80	
	R1:2	1.57	716.50	40.90	35.28	
	R1:3	2.05	335.75	56.65	52.65	
	R1:4	2.33	265.00	52.73	49.53	
	R1:5	2.50	195.30	51.88	50.95	
	R1:6	2.72	165.68	46.48	47.48	
	R1:7	2.51	142.05	34.08	35.80	
	R1:8	2.49	122.98	27.13	29.28	
	R1:9	2.43	109.70	22.83	25.78	
	R1:10	2.40	111.15	17.04	19.55	
	R1:11	2.43	82.03	11.95	14.10	
	R1:12	2.29	77.13	8.36	10.16	
	R1:13	2.94	73.30	5.83	7.37	
	R1:14	1.59	52.40	2.16	2.47	



Mass Balance	Inintial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	Dry weight (mg)	PGM (mg)
Pt	5.54	8.00	44.31	8.00	0.69	8.00	5.54
Pd	5.06	8.00	40.46	8.00	0.63	8.00	5.06
Au	9.38	8.00	75.07	8.00	1.17	8.00	9.38

Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.13	0.00	0.11	0.00	0.01	0.00
8.40	0.60	0.30	2.49	0.26	1.96	0.01	0.10
16.80	1.20	0.41	8.38	0.37	6.60	0.02	0.31
25.20	1.80	0.46	16.49	0.43	13.28	0.02	0.53
33.60	2.40	0.44	25.59	0.42	21.04	0.02	0.81
42.00	3.00	0.41	34.29	0.41	28.67	0.02	1.11
50.40	3.60	0.34	42.47	0.35	36.14	0.02	1.44
58.80	4.20	0.26	49.17	0.27	42.47	0.02	1.76
67.20	4.80	0.21	54.26	0.23	47.41	0.02	2.08
75.60	5.40	0.25	58.41	0.29	51.59	0.03	2.39
88.20	6.30	0.24	63.39	0.28	56.75	0.04	2.84
105.00	7.50	0.26	68.21	0.31	61.86	0.06	3.45
130.20	9.30	0.24	73.27	0.29	67.39	0.09	4.33
163.80	11.70	0.13	77.99	0.17	72.72	0.08	5.65
197.40	14.10		80.65		75.71		6.78
Sum		**4.07**		**4.19**		**0.45**	



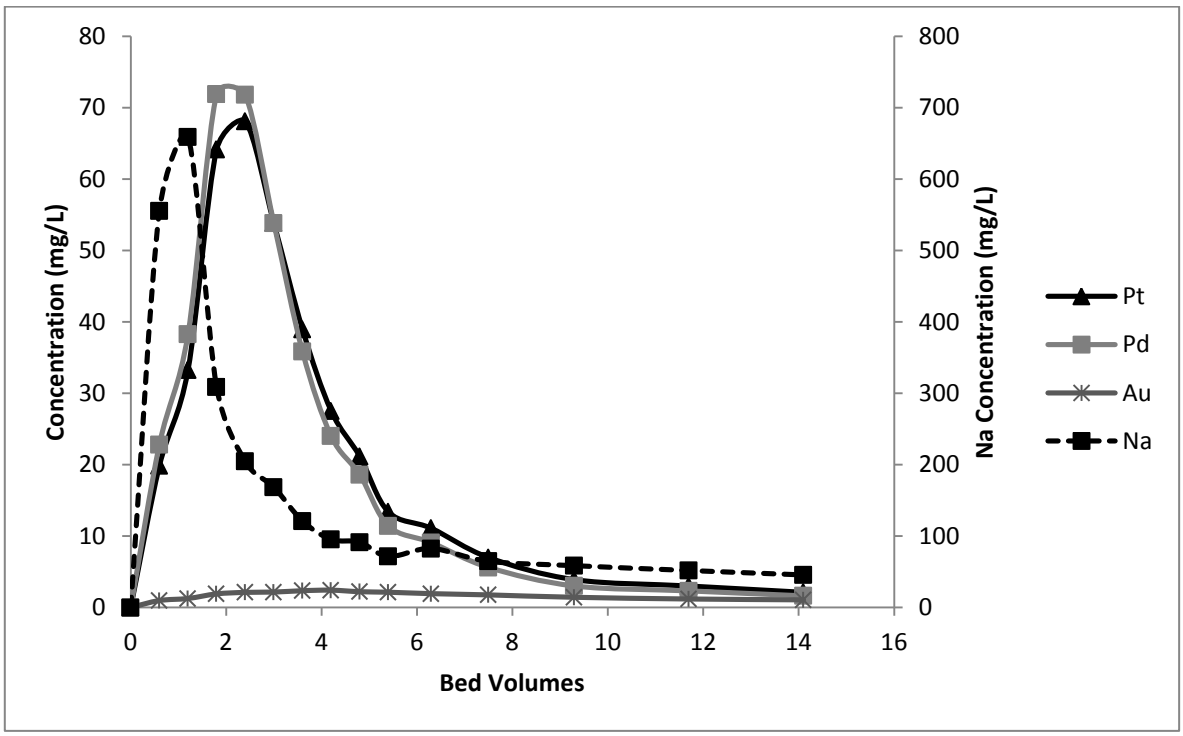
Elution experiment Repeat 2

Loading experiment I

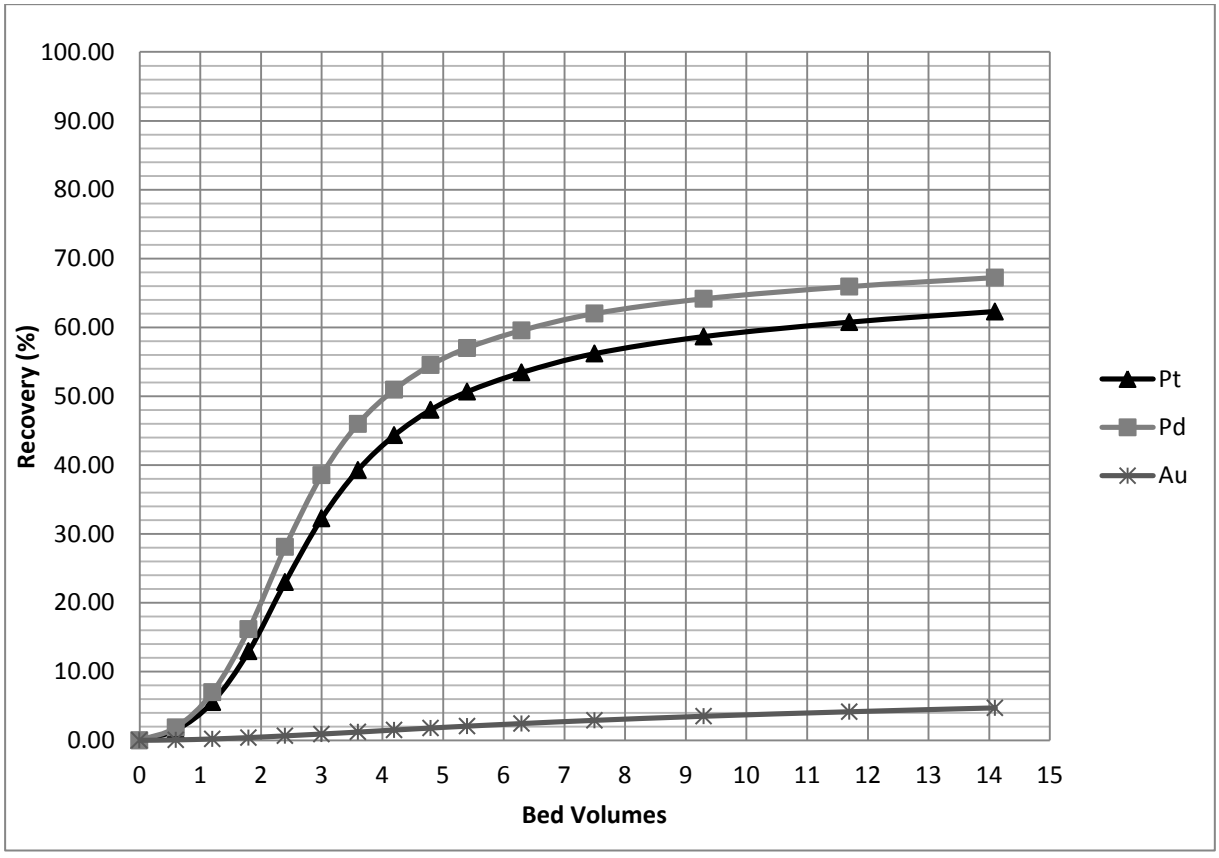
Date		
Pre-treatment step		**wt %**
NaOH (g)	0.22	0.55
NaCN (g)	0	0
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	
Flow rate (BV/hr)	3.6

	mg/L	**Au**	**Na**	**Pd**	**Pt**	**Sample Time**
pre-treatment		0.02	2151.75	0.10	0.10	The times for the first runs were not taken but they were more or less 10min for the first 9 and then as discussed in increments of 5, 10, 20, 30 and 40 min
water		0.06	10.54	0.02	0.02	
1	**R2:1**	0.97	555.25	22.78	19.82	
2	**R2:2**	1.26	658.75	38.28	33.25	
3	**R2:3**	1.90	308.50	71.90	64.13	
4	**R2:4**	2.11	204.58	71.78	68.08	
5	**R2:5**	2.15	168.50	53.80	53.83	
6	**R2:6**	2.34	120.90	35.83	38.95	
7	**R2:7**	2.42	95.40	24.01	27.53	
8	**R2:8**	2.20	91.43	18.60	21.15	
9	**R2:9**	2.13	71.30	11.41	13.38	
10	**R2:10**	1.93	82.50	9.09	11.08	
11	**R2:11**	1.76	64.63	5.61	6.99	
12	**R2:12**	1.42	58.48	3.01	3.89	
13	**R2:13**	1.18	51.70	2.32	3.00	
14	**R2:14**	1.06	45.53	1.62	2.12	



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.10	0.00	0.08	0.00	0.00	0.00
8.40	0.60	0.26	1.89	0.22	1.51	0.01	0.06
16.80	1.20	0.46	6.97	0.41	5.54	0.01	0.20
25.20	1.80	0.60	16.14	0.56	12.93	0.02	0.40
33.60	2.40	0.53	28.08	0.51	22.97	0.02	0.65
42.00	3.00	0.38	38.53	0.39	32.23	0.02	0.92
50.40	3.60	0.25	45.98	0.28	39.28	0.02	1.20
58.80	4.20	0.18	50.96	0.20	44.32	0.02	1.50
67.20	4.80	0.13	54.50	0.15	48.02	0.02	1.79
75.60	5.40	0.13	57.00	0.15	50.64	0.03	2.06
88.20	6.30	0.12	59.55	0.15	53.43	0.03	2.44
105.00	7.50	0.11	62.00	0.14	56.18	0.04	2.90
130.20	9.30	0.09	64.15	0.12	58.65	0.04	3.50
163.80	11.70	0.07	65.92	0.09	60.75	0.04	4.15
197.40	14.10		67.23		62.30		4.71
Sum (mg)		**3.39**		**3.45**		**0.32**	



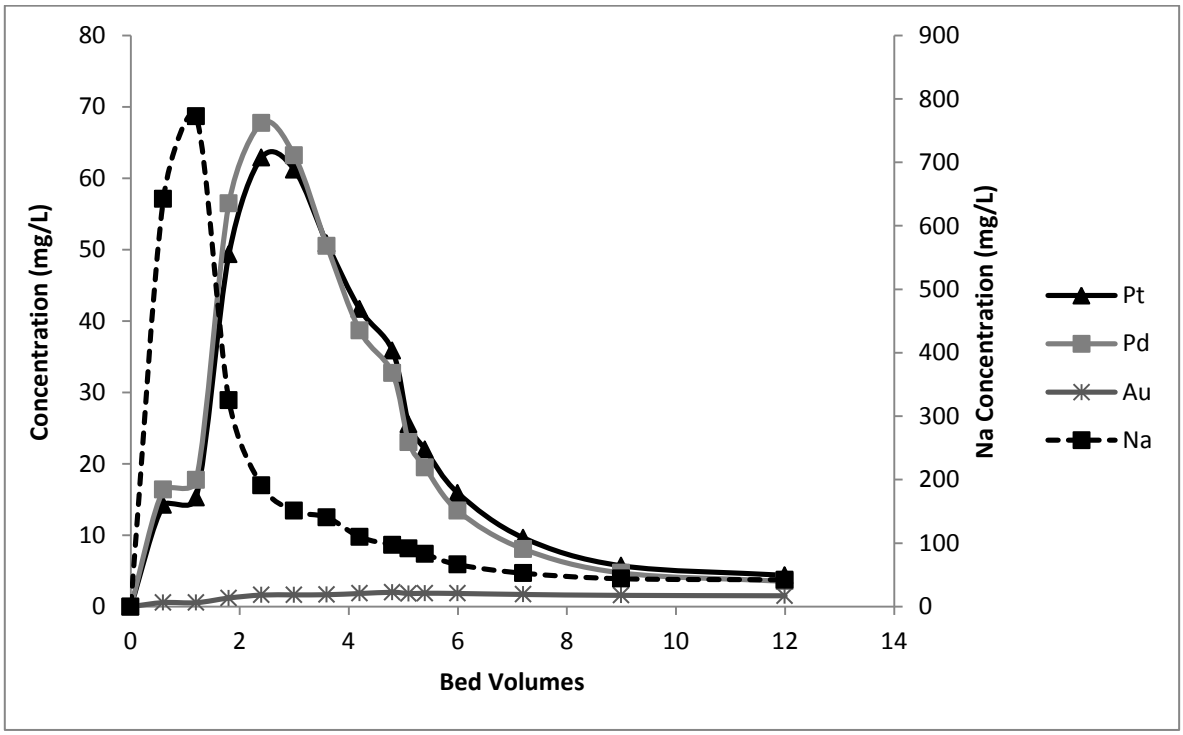
Elution experiment Repeat 3

Loading experiment I

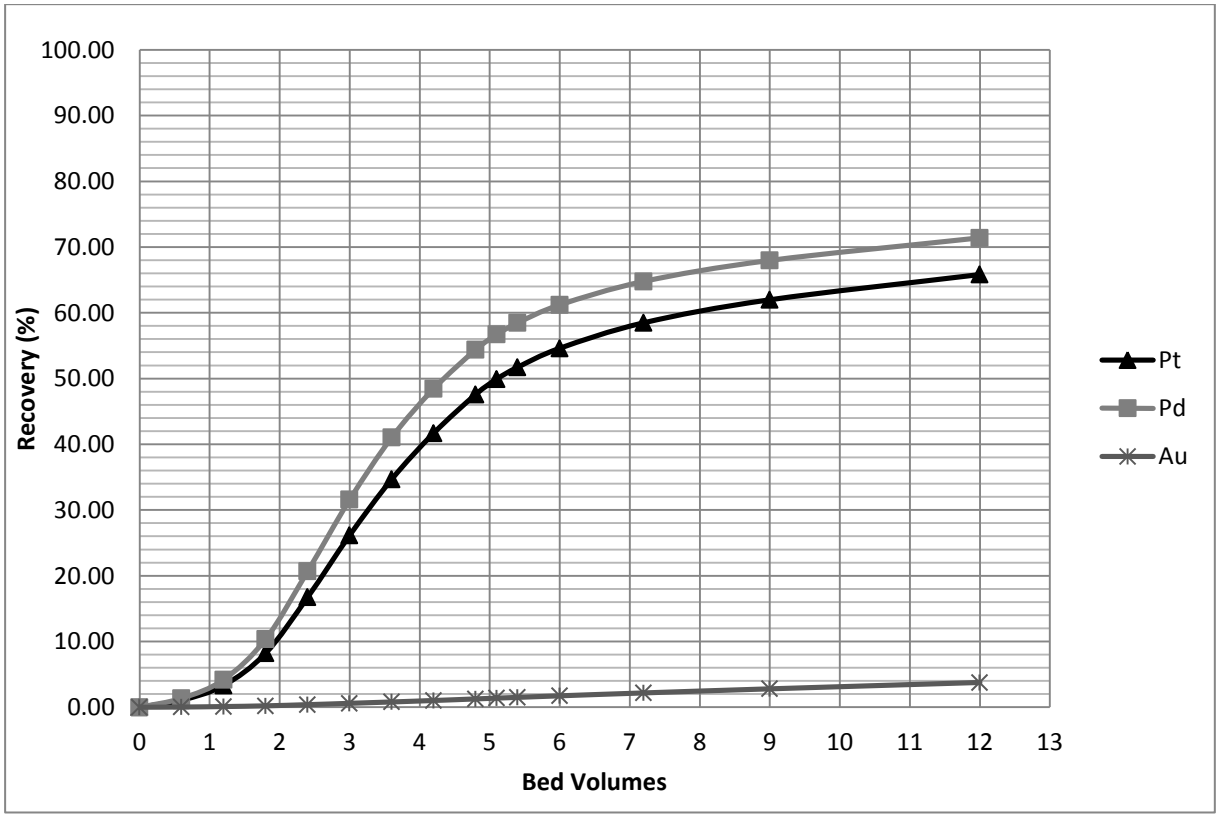
Date		
Pre-treatment step		**wt %**
NaOH (g)	0.22	0.55
NaCN (g)	0	0
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	
Flow rate (BV/hr)	3.6

	mg/L	**Au**	**Na**	**Pd**	**Pt**	**Sample stop**
pre-treatment						
water		nd	14.03	nd	nd	
	R3:1	0.57	642.50	16.39	14.22	12:00
	R3:2	0.55	772.25	17.72	15.26	12:07
	R3:3	1.21	325.25	56.45	49.33	12:18
	R3:4	1.62	191.00	67.73	62.88	12:30
	R3:5	1.65	150.88	63.18	61.18	12:42
	R3:6	1.67	140.70	50.50	50.85	12:51
	R3:7	1.84	109.75	38.65	41.65	13:00
	R3:8	2.01	97.33	32.70	35.85	13:11
	R3:9	1.83	91.38	23.04	25.55	13:16
	R3:10	1.88	82.75	19.46	22.01	13:21
	R3:11	1.84	66.13	13.41	15.90	13:32
	R3:12	1.71	52.63	8.07	9.64	13:52
	R3:13	1.58	43.93	4.72	5.72	14:22
	R3:14	1.52	42.28	3.55	4.39	15:08



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.07	0.00	0.06	0.00	0.00	0.00
8.40	0.60	0.14	1.36	0.12	1.08	0.00	0.04
16.80	1.20	0.31	4.20	0.27	3.32	0.01	0.11
25.20	1.80	0.52	10.37	0.47	8.22	0.01	0.22
33.60	2.40	0.55	20.69	0.52	16.74	0.01	0.39
42.00	3.00	0.48	31.58	0.47	26.17	0.01	0.60
50.40	3.60	0.37	41.04	0.39	34.67	0.01	0.81
58.80	4.20	0.30	48.45	0.33	41.70	0.02	1.03
67.20	4.80	0.12	54.38	0.13	47.59	0.01	1.27
71.40	5.10	0.09	56.70	0.10	49.92	0.01	1.39
75.60	5.40	0.14	58.47	0.16	51.72	0.02	1.50
84.00	6.00	0.18	61.20	0.21	54.60	0.03	1.74
100.80	7.20	0.16	64.78	0.19	58.48	0.04	2.18
126.00	9.00	0.17	67.96	0.21	61.98	0.07	2.80
168.00	12.00		71.40		65.82		3.77
Sum (mg)		**3.61**		**3.64**		**0.25**	



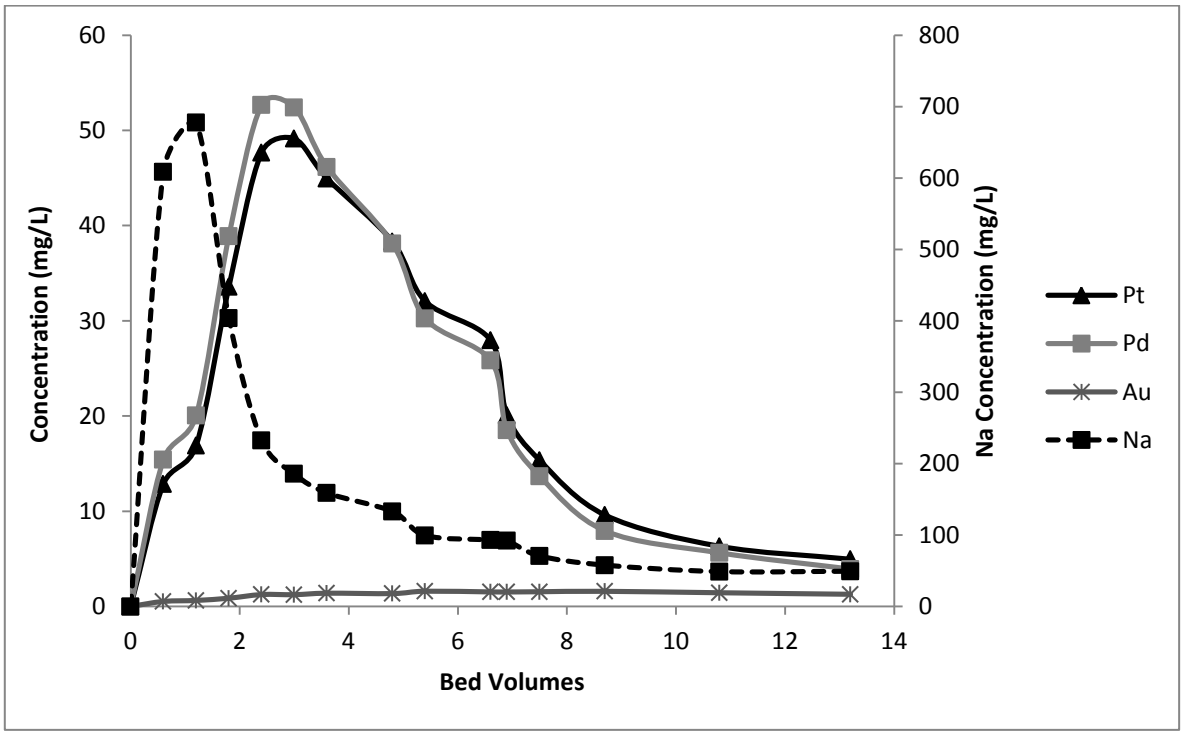
Elution experiment Repeat 4

Loading experiment I

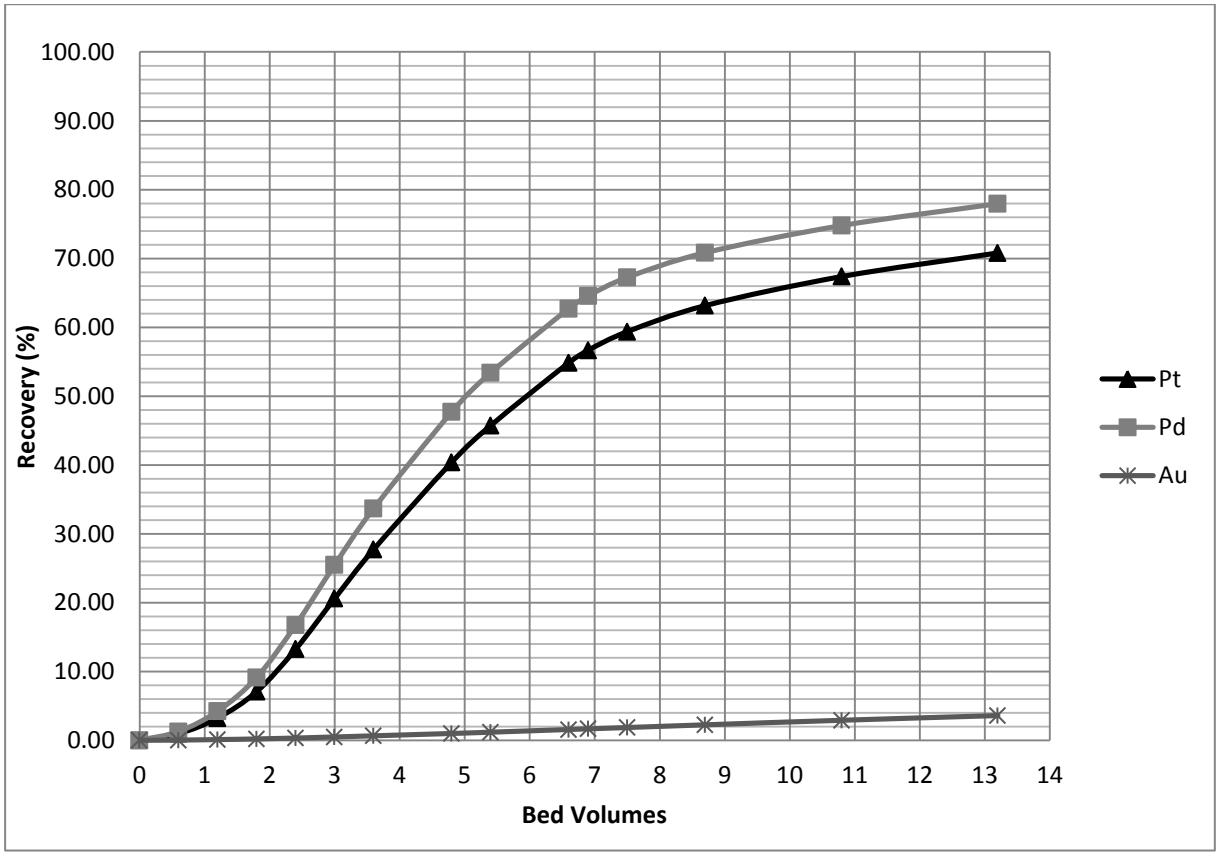
Date		
Pre-treatment step		**wt %**
NaOH (g)	0.22	0.55
NaCN (g)	0	0
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14
pH after	
Flow rate (BV/hr)	3.6

	mg/L	Au	Na	Pd	Pt	Sample stop
pre-treatment						
water		nd	14.03	nd	nd	
	R4 5:1	0.52	608.75	15.42	12.87	12:21
	R4 5:2	0.63	677.50	20.06	16.91	12:31
	R4 5:3	0.87	403.75	38.90	33.58	12:43
	R4 5:4	1.25	232.50	52.68	47.68	12:49
	R4 5:5	1.24	185.63	52.40	49.13	13:02
	R4 5:6	1.39	158.93	46.15	44.95	12:12
	R4 5:7	1.35	132.93	38.13	38.33	13:30
	R4 5:8	1.60	99.45	30.25	32.05	13:40
	R4 5:9	1.52	93.25	25.85	27.95	13:58
	R4 5:10	1.52	92.18	18.51	20.09	14:05
	R4 5:11	1.54	70.70	13.67	15.34	14:15
	R4 5:12	1.59	57.80	7.93	9.59	14:37
	R4 5:13	1.44	48.78	5.63	6.31	15:09
	R4 5:14	1.28	49.30	3.93	4.96	15:50



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.06	0.00	0.05	0.00	0.00	0.00
8.40	0.60	0.15	1.28	0.13	0.98	0.00	0.03
16.80	1.20	0.25	4.23	0.21	3.24	0.01	0.10
25.20	1.80	0.38	9.14	0.34	7.07	0.01	0.20
33.60	2.40	0.44	16.75	0.41	13.24	0.01	0.33
42.00	3.00	0.41	25.49	0.40	20.59	0.01	0.49
50.40	3.60	0.71	33.69	0.70	27.74	0.02	0.65
67.20	4.80	0.29	47.70	0.30	40.39	0.01	0.99
75.60	5.40	0.47	53.39	0.50	45.73	0.03	1.18
92.40	6.60	0.09	62.72	0.10	54.85	0.01	1.57
96.60	6.90	0.14	64.57	0.15	56.67	0.01	1.66
105.00	7.50	0.18	67.24	0.21	59.36	0.03	1.86
121.80	8.70	0.20	70.84	0.23	63.15	0.04	2.25
151.20	10.80	0.16	74.78	0.19	67.38	0.05	2.91
184.80	13.20		77.96		70.80		3.59
Sum (mg)		**3.94**		**3.92**		**0.24**	



Elution experiments AG – AJ

Elution dependence on water quality

Loading experiment E

Mass Balance	Inintial solution (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	AC dry weight (mg)	PGM (mg)
Pt	4.58	4.00	18.33	8	0.57	8	4.583
Pd	4.19	4.00	16.75	8	0.52	8	4.187
Au	5.44	4.00	21.76	8	0.68	8	5.441

Date	6-7 March 2012	
Pre-treatment step		**wt %**
NaoH (g)	0.22	0.55
NaCN (g)	0.8	2
Volume (mL)	40	
Stirred (min)	30	
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	14

		Au	**Na**	**Pd**	**Pt**	**Sample volume (mL)**
Quality Control	**Cert std value**	0.96		0.96	0.96	
	Analysed	0.94		0.91	0.97	
	% Error	1.81		4.92	0.88	
Water	**AI 1**	nd	80.32	nd	nd	
Water	**AJ 1**	nd	186.70	nd	nd	
Water	**AG 1**	nd	154.20	nd	nd	
Water	**AH 1**	nd	301.00	nd	nd	
Eluant	**AI 2**	3.49	876.80	48.67	51.71	77.5
Eluant	**AJ 2**	3.03	1104.00	49.99	53.28	74
Eluant	**AG 2**	3.62	947.70	51.91	55.84	70
Eluant	**AH 2**	2.69	1109.00	47.63	50.03	72

		Au	**Pd**	**Pt**	**Au**	**Pd**	**Pt**
	BV	**Weight (mg)**			**recovery %**		
AI 2	5.5	0.27	3.77	4.01	5	90	87
AJ 2	5.3	0.22	3.70	3.94	4	88	86
AG 2	5.0	0.25	3.63	3.91	5	87	85
AH 2	5.1	0.19	3.43	3.60	4	82	79

Elution experiments AL

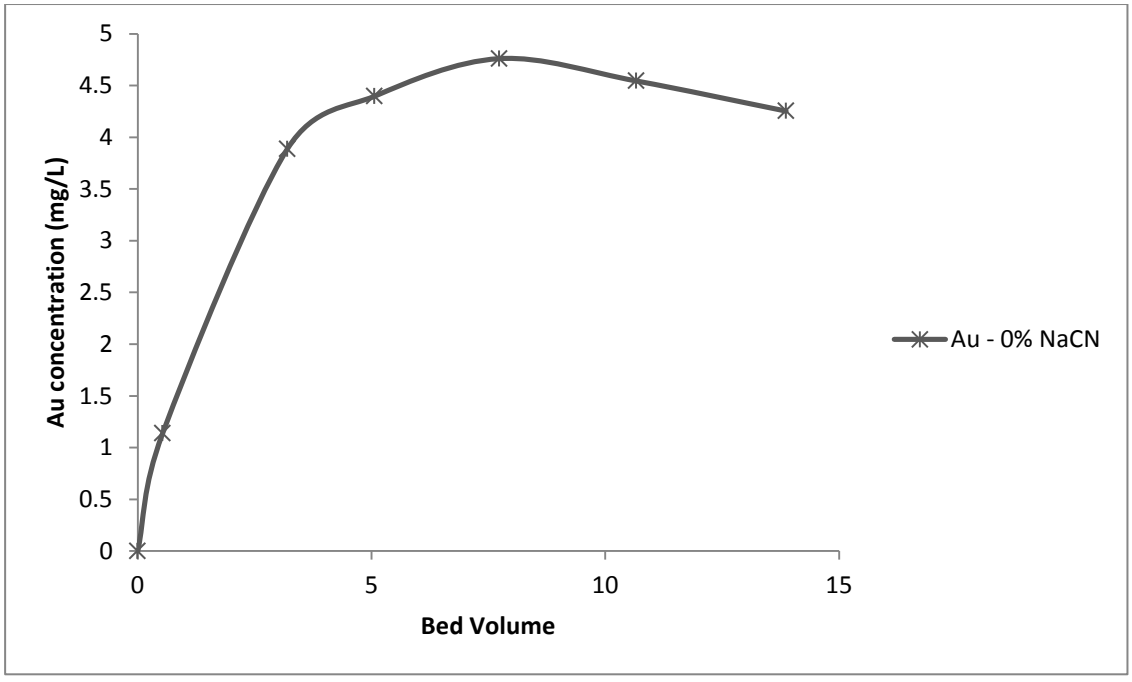
Single component gold elution

Loading experiment F

Date		
Pre-treatment step		**wt %**
NaOH (g)	0.2	0.55
NaCN (g)	0	0
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

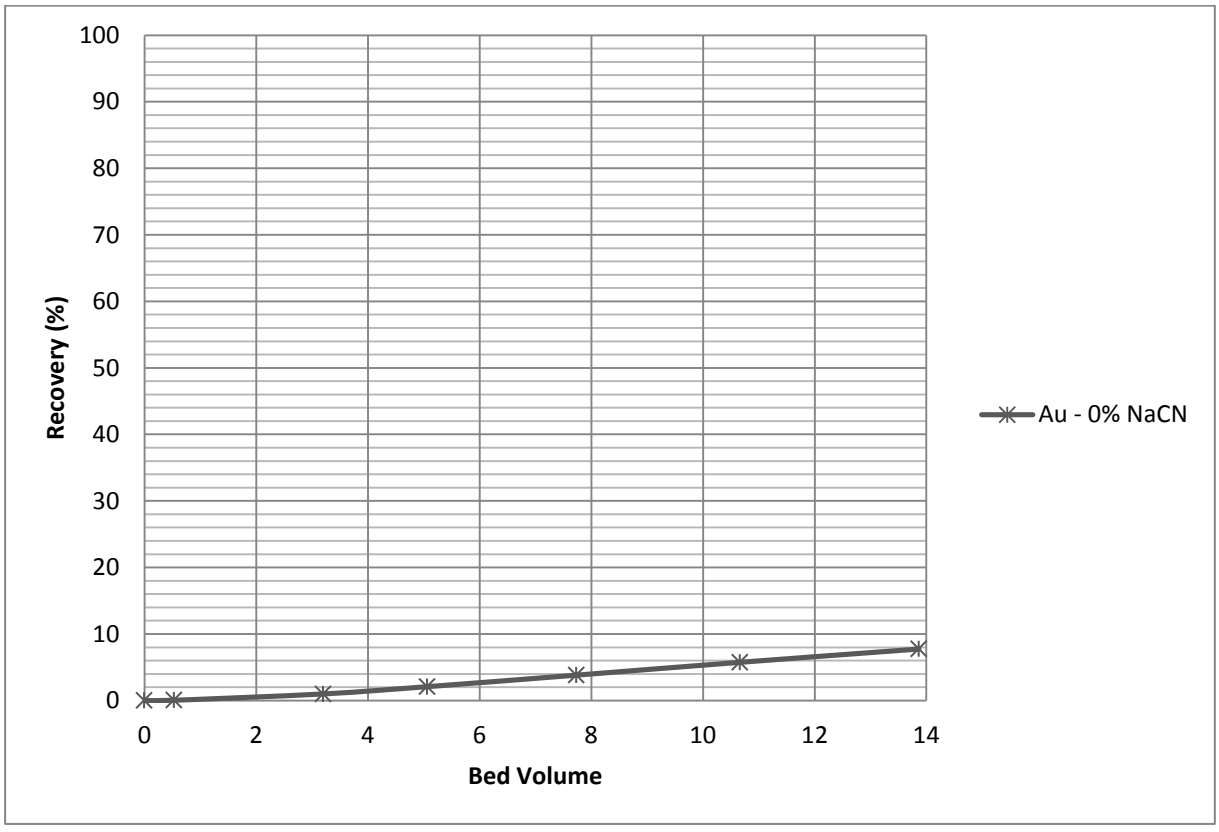
Elution	
Temperature (°C)	80
Bed Volume (mL)	13
pH after	
Flow rate (BV/hr)	3.2

	Au (mg/L)	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
1 mg/L Au QC	1.03					
AL2	0.60					
AL3	1.14	5.80	10:02	10:10	8	3.35
AL3	0.98					
AL3	1.02					
AL4	3.89	7.80	10:48	11:00	12	3.00
AL3	1.00					
AL5	4.40			11:35		
AL6	4.76			12:25		
AL7	4.54			13:21		
AL8	4.25			14:22		



Mass Balance	Au adsorbed (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	Au (mg)
Au	9.17	2.00	18.34	8	1.15	9.17

Time (s)	BV	Au (mg)	Recovery (%)
0.00	0.00	0.00	0.00
6.93	0.53	0.09	0.04
41.60	3.20	0.10	0.99
65.87	5.07	0.16	2.09
100.53	7.73	0.18	3.82
138.67	10.67	0.18	5.75
180.27	13.87		7.75
Total Au (mg)		**9.17**	



Elution experiments AM

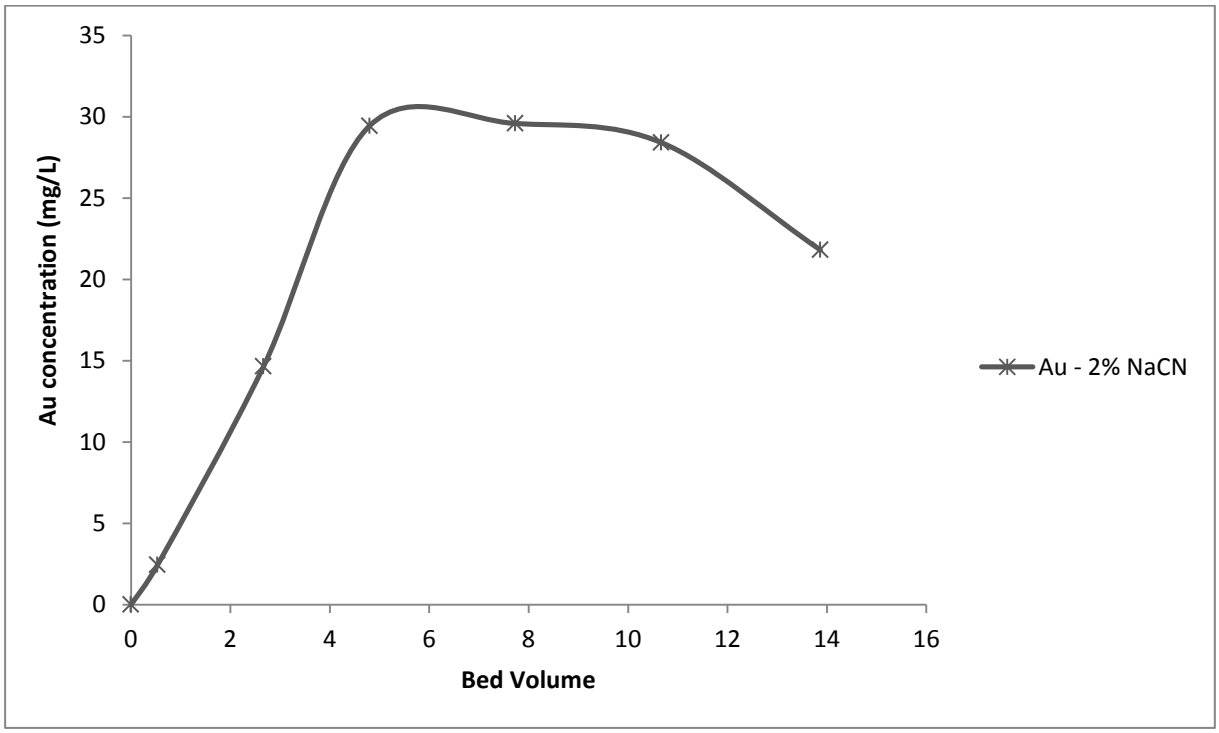
Single component gold elution

Loading experiment F

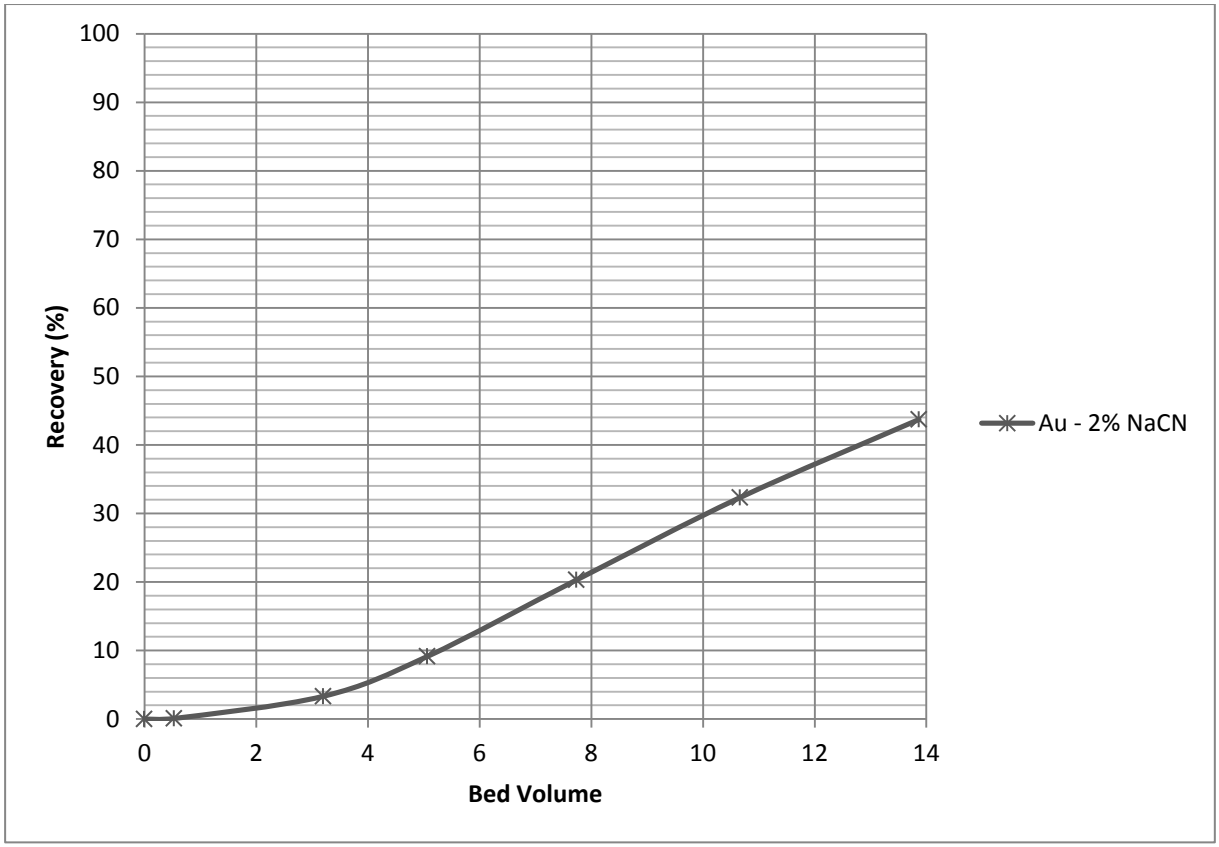
Date		
Pre-treatment step		**wt %**
NaOH (g)	0.2	0.55
NaCN (g)	8	2
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	12	

Elution	
Temperature (°C)	80
Bed Volume (mL)	12
pH after	
Flow rate (BV/hr)	2.1

	Au	Sample Volume (mL)	Sample Start	Sample stop	Time (min)	Flow rate (BV/hr)
1 mg/L Au QC	1.03					
AM2	0.00					
AM3	2.44			11:08		
AM4	14.65			11:52		
AM5	29.44			12:28		
AM6	29.58			13:25		
AM7	28.41			14:21		
AM8	21.81			15:22		



Time (s)	BV	Au (mg)	Recovery (%)
0.00	0.00	0.01	0.00
6.93	0.53	0.30	0.09
34.67	2.67	0.53	3.32
62.40	4.80	1.02	9.15
100.53	7.73	1.11	20.29
138.67	10.67	1.04	32.33
180.27	13.87		43.71
Sum Au (mg)			**9.17**



Elution experiments ACID 1 - 5

Loading experiment G

Date	3 – 5 April 2012	
Pre-treatment step		**wt %**
NaOH (g)	0.2	0.55
NaCN (g)	0.8	2
Volume (mL)	40	
Stirred (min)	30	
pH		
Activated Carbon (wet g)	11	

Elution	
Temperature (°C)	80
Bed Volume (mL)	12
pH after	
Flow rate (BV/hr)	

		Elution start	Elution Stop	Time (min)	Volume (mL)	Flow rate (BV/hr)
Acid 1	**1M cold**	11:33	12:40	67	67.5	4.65
Acid 2	**3 M cold**	11:00	12:53	113	67.3	2.75
Acid 3	**1M hot**	11:58	13:28	90	75	3.85
Acid 4	**3 M hot**	10:46	11:51	65	66	4.69
Acid 5	**not acid**	11:46	12:46	60	67	5.15

		Au	Na	Pd	Pt	Cu	Ni
Quality Control	**Cert std**						
	value	1.96	9.8				
	Analysed	1.91	11.78				
	% Error	2.40	20.20				
	ACID1	nd	424.7	nd	< 0.05	0.38	0.82
	Water 1	nd	28.92	nd	< 0.05	0.12	0.19
1 M COLD	**Elute 1**	5.40	894.8	29.67	35.35	130.60	456.00
	ACID 2	nd	449.6	nd	< 0.05	0.12	2.96
	Water 2	< 0.05	28.4	nd	< 0.05	0.04	0.46
3 M COLD	**Elute 2**	3.73	1025	33.60	39.80	127.20	466.10
	ACID 3	nd	490.2	nd	< 0.05	3.45	614.30
	Water 3	nd	30.82	nd	< 0.05	0.25	40.39
1 M HOT	**Elute 3**	8.61	883	31.78	38.57	134.60	132.60
	ACID 4	nd	486.8	nd	< 0.05	7.68	721.60
	Water 4	nd	26.39	nd	< 0.05	0.48	35.16
3 M HOT	**Elute 4**	9.16	769.4	33.00	40.46	111.10	75.53
NONE	**Elute 5**	3.25	1209	29.03	34.05	128.30	468.20

Mass Balance	Adsorbed (mg/L)	Solution amount (l)	Metal in solution (mg)	AC conc (g/L)	Loading on AC(mg/g)	Dry AC (g)	AC loading (mg/g)
Pt	3.99	4	15.96	8	0.50	6.4	3.19
Pd	3.17	4	12.67	8	0.40	6.4	2.53
Au	6.58	4	26.30	8	0.82	6.4	5.26
Cu	4.58	4	18.32	8	0.57	6.4	3.66
Ni	44.73	4	178.92	8	5.59	6.4	35.78

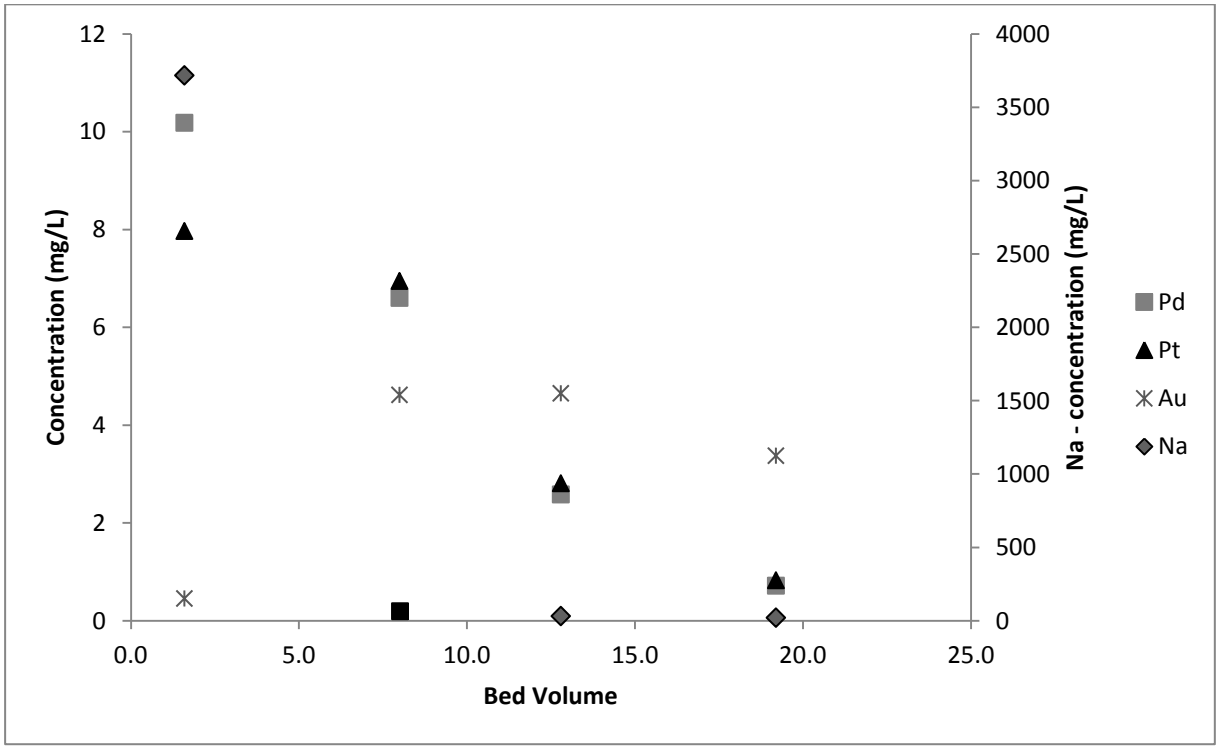
First elution experiment

From carbon loading experiment 1.

Date	
Pre-treatment step	
NaoH (%)	0.55
NaCN (%)	2
Volume (mL)	40
Stirred (min)	30
pH	13.44
Activated Carbon (g)	8.38

Elution	
Temperature (°C)	70
Bed Volume (mL)	13
pH after	11.33
Flow rate (BV/hr)	9.6

Values in ppb (µg/L)					Na	Pd	Pt	Au
Quality Control	**Sample Volume (mL)**	**Time**	**Sampling time (min)**	**Cert std value**	20230			98
				Measured	18063			99
				Error (%)	11			1
Pre-treatment sample	10			**N1**	11201512	59.7	34	9
	10	13:15		**N2**	3716347	10178.5	7965	456
	10	13:52	04:50	**N5**	65967	6597.0	6944	4614
	10	14:20		**N7**	32180	2581.4	2807	4647
	9.6	15:02		**N9**	19374	713.7	824	3374
Bulk sample	10			**N11**	144878	9493.8	9668	3952



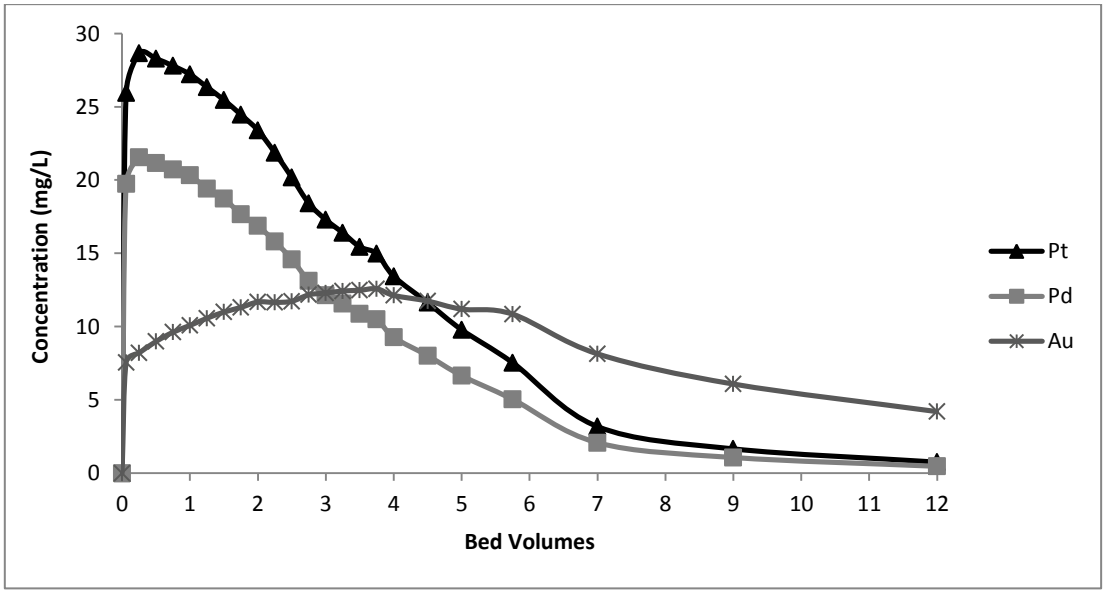
Elution experiment T1

From carbon loading experiment J

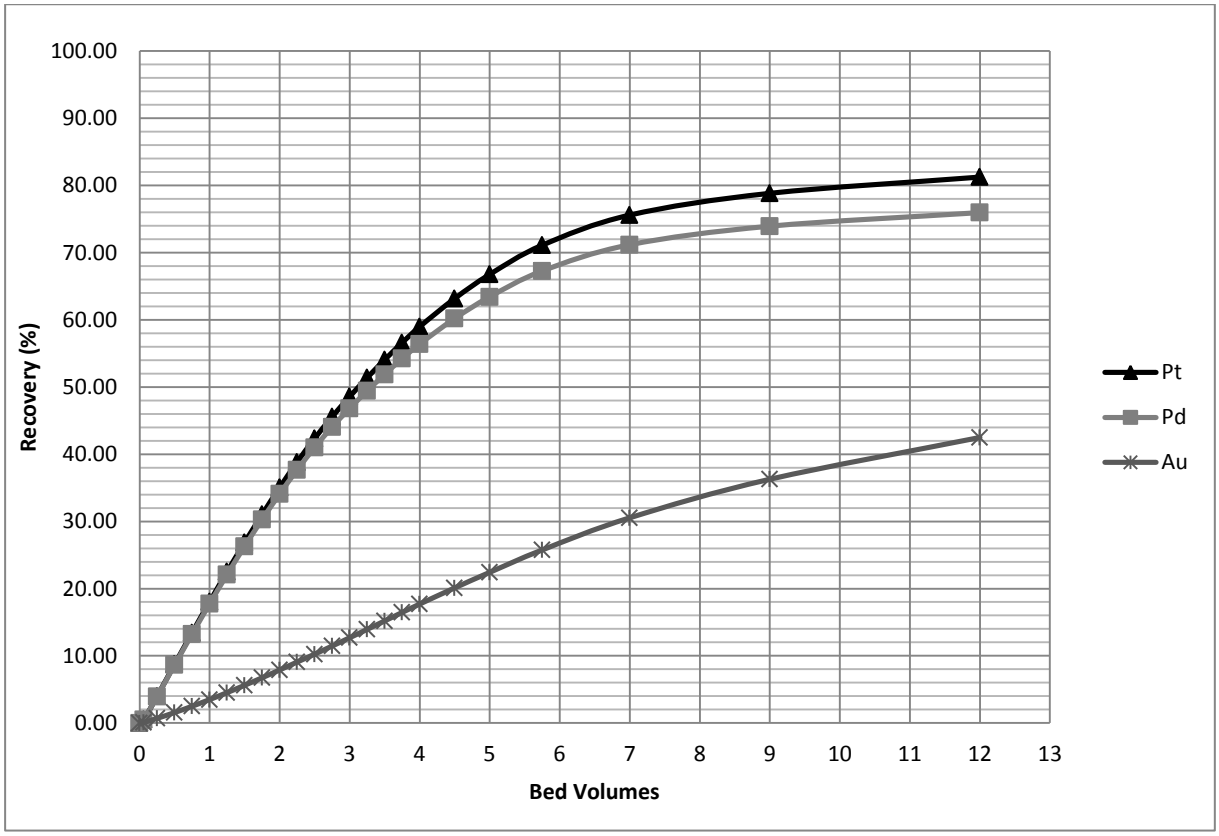
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature	25

Elution	
Temperature (C)	100
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**100 L T1**	7.56	19.73	25.94
0.25	**100 L T2**	8.20	21.54	28.65
0.50	**100 L T3**	8.99	21.15	28.28
0.75	**100 L T4**	9.62	20.73	27.79
1.00	**100 L T5**	10.08	20.33	27.21
1.25	**100 L T6**	10.57	19.40	26.34
1.50	**100 L T7**	10.99	18.74	25.46
1.75	**100 L T8**	11.31	17.66	24.46
2.00	**100 L T9**	11.68	16.87	23.39
2.25	**100 L T10**	11.65	15.81	21.86
2.50	**100 L T11**	11.73	14.59	20.17
2.75	**100 L T12**	12.17	13.11	18.41
3.00	**100 L T13**	12.29	12.13	17.29
3.25	**100 L T14**	12.43	11.57	16.40
3.50	**100 L T15**	12.48	10.87	15.44
3.75	**100 L T16**	12.58	10.49	14.97
4.00	**100 L T17**	12.13	9.27	13.43
4.50	**100 L T18**	11.74	8.02	11.63
5.00	**100 L T19**	11.19	6.65	9.78
5.75	**100 L T20**	10.85	5.04	7.54
7.00	**100 L T21**	8.14	2.08	3.18
9.00	**100 L T22**	6.08	1.07	1.66
12.00	**100 L T23**	4.20	0.47	0.75



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.05	0.00	0.06	0.00	0.02	0.00
4.80	0.06	0.31	0.52	0.41	0.52	0.12	0.09
20.00	0.25	0.43	3.96	0.57	3.99	0.17	0.70
40.00	0.50	0.42	8.65	0.56	8.76	0.19	1.56
60.00	0.75	0.41	13.25	0.55	13.45	0.20	2.50
80.00	1.00	0.40	17.75	0.54	18.05	0.21	3.49
100.00	1.25	0.38	22.11	0.52	22.53	0.22	4.53
120.00	1.50	0.36	26.30	0.50	26.87	0.22	5.62
140.00	1.75	0.35	30.30	0.48	31.04	0.23	6.74
160.00	2.00	0.33	34.09	0.45	35.05	0.23	7.90
180.00	2.25	0.30	37.67	0.42	38.84	0.23	9.08
200.00	2.50	0.28	41.01	0.39	42.35	0.24	10.26
220.00	2.75	0.25	44.05	0.36	45.58	0.24	11.46
240.00	3.00	0.24	46.82	0.34	48.57	0.25	12.69
260.00	3.25	0.22	49.42	0.32	51.39	0.25	13.94
280.00	3.50	0.21	51.89	0.30	54.05	0.25	15.20
300.00	3.75	0.20	54.23	0.28	56.60	0.25	16.46
320.00	4.00	0.35	56.40	0.50	58.97	0.48	17.70
360.00	4.50	0.29	60.20	0.43	63.17	0.46	20.11
400.00	5.00	0.35	63.42	0.52	66.75	0.66	22.42
460.00	5.75	0.36	67.27	0.54	71.10	0.95	25.75
560.00	7.00	0.25	71.17	0.39	75.58	1.14	30.54
720.00	9.00	0.18	73.93	0.29	78.82	1.23	36.27
960.00	12.00		75.95		81.24		42.49



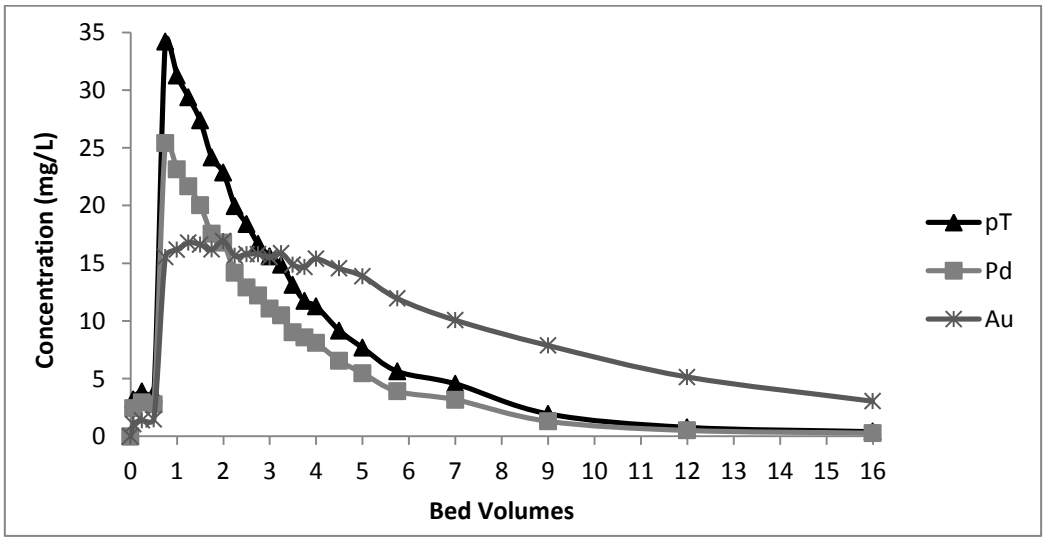
Elution experiment T2

From carbon loading experiment J

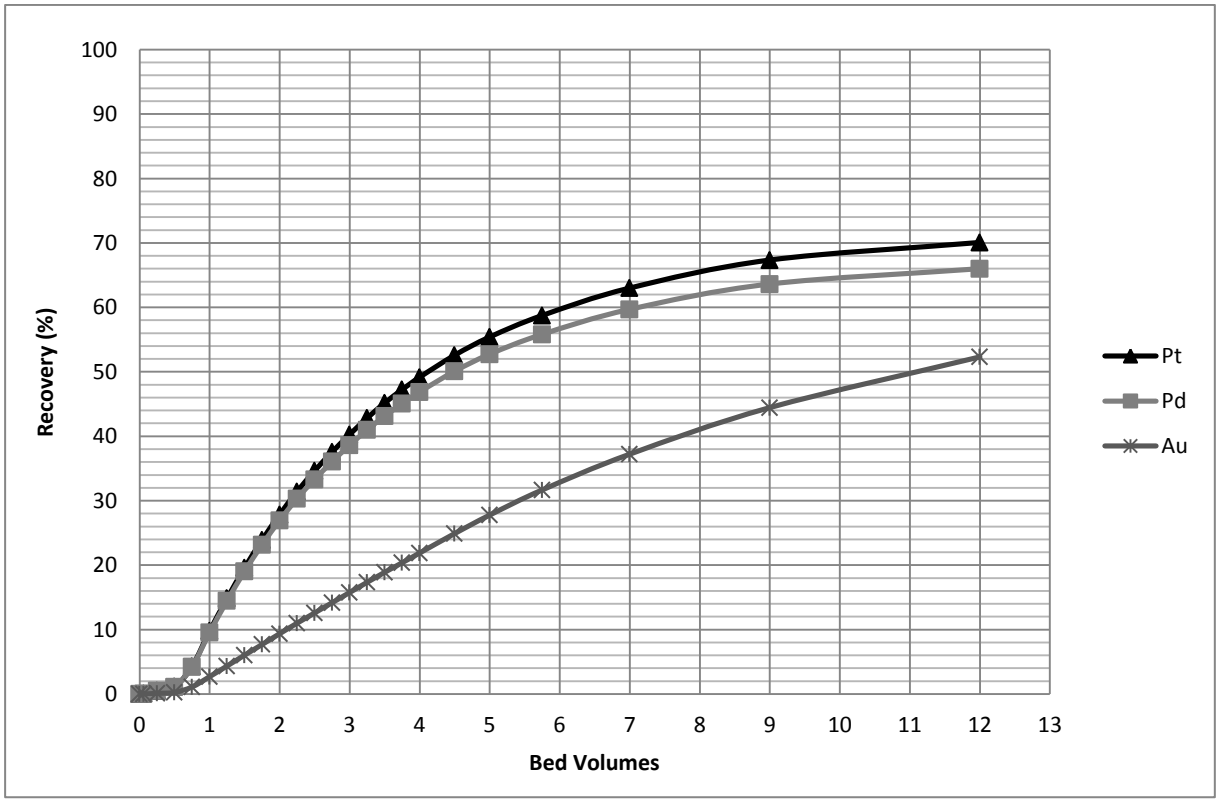
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	25

Elution	
Temperature (°C)	110
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**110 L T1**	1.05	2.43	3.19
0.25	**110 L T2**	1.37	2.94	3.87
0.50	**110 L T3**	1.47	2.78	3.68
0.75	**110 L T4**	15.53	25.41	34.19
1.00	**110 L T5**	16.16	23.14	31.27
1.25	**110 L T6**	16.77	21.66	29.37
1.50	**110 L T7**	16.62	20.03	27.37
1.75	**110 L T8**	16.19	17.56	24.16
2.00	**110 L T9**	16.91	16.78	22.85
2.25	**110 L T10**	15.63	14.17	19.93
2.50	**110 L T11**	15.78	12.89	18.40
2.75	**110 L T12**	15.79	12.19	16.68
3.00	**110 L T13**	15.53	11.06	15.58
3.25	**110 L T14**	15.85	10.49	14.86
3.50	**110 L T15**	14.86	9.02	13.12
3.75	**110 L T16**	14.68	8.56	11.72
4.00	**110 L T17**	15.38	8.09	11.26
4.50	**110 L T18**	14.55	6.54	9.16
5.00	**110 L T19**	13.86	5.47	7.67
5.75	**110 L T20**	11.94	3.90	5.63
7.00	**110 L T21**	10.06	3.17	4.55
9.00	**110 L T22**	7.87	1.30	1.94
12.00	**110 L T23**	5.14	0.51	0.77
16.00	**110 L T24**	3.04	0.28	0.40



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
4.80	0.06	0.04	0.06	0.05	0.06	0.02	0.01
20.00	0.25	0.06	0.51	0.08	0.51	0.03	0.11
40.00	0.50	0.28	1.14	0.38	1.14	0.17	0.25
60.00	0.75	0.49	4.23	0.65	4.31	0.32	1.11
80.00	1.00	0.45	9.56	0.61	9.79	0.33	2.70
100.00	1.25	0.42	14.48	0.57	14.87	0.33	4.36
120.00	1.50	0.38	19.06	0.52	19.61	0.33	6.05
140.00	1.75	0.34	23.18	0.47	23.93	0.33	7.70
160.00	2.00	0.31	26.95	0.43	27.86	0.33	9.37
180.00	2.25	0.27	30.35	0.38	31.44	0.31	11.01
200.00	2.50	0.25	33.32	0.35	34.65	0.32	12.59
220.00	2.75	0.23	36.07	0.32	37.58	0.31	14.18
240.00	3.00	0.22	38.63	0.30	40.28	0.31	15.76
260.00	3.25	0.20	40.99	0.28	42.83	0.31	17.34
280.00	3.50	0.18	43.13	0.25	45.17	0.30	18.89
300.00	3.75	0.17	45.06	0.23	47.25	0.30	20.38
320.00	4.00	0.29	46.89	0.41	49.17	0.60	21.89
360.00	4.50	0.24	50.10	0.34	52.59	0.57	24.91
400.00	5.00	0.28	52.74	0.40	55.41	0.77	27.77
460.00	5.75	0.35	55.82	0.51	58.75	1.10	31.68
560.00	7.00	0.36	59.70	0.52	63.01	1.43	37.22
720.00	9.00	0.22	63.62	0.33	67.35	1.56	44.45
960.00	12.00	0.13	66.01	0.19	70.08	1.31	52.32
1280.00	16.00		67.38		71.65		58.91
Sum (mg)		**6.01**		**8.37**		**10.38**	



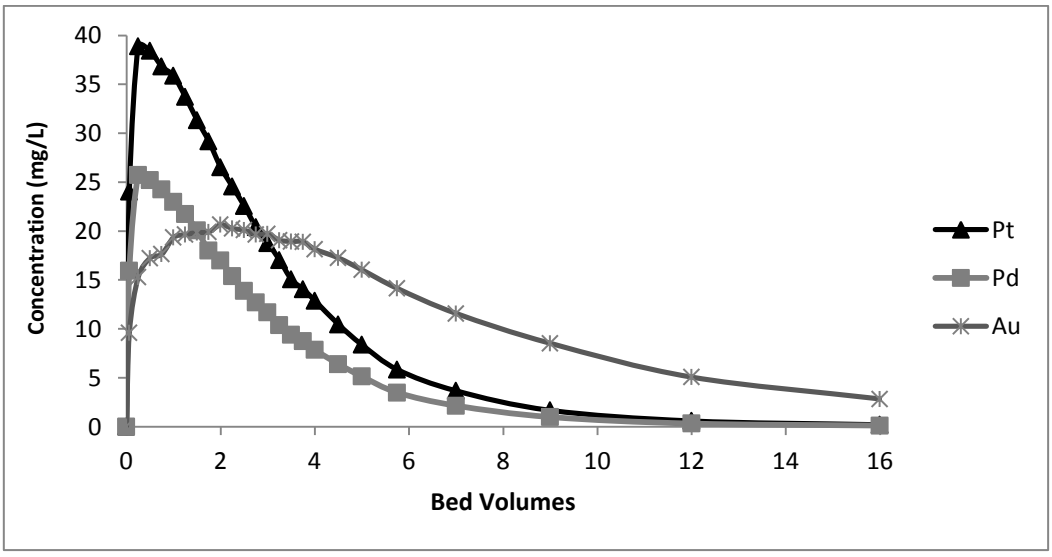
Elution experiment T3

From carbon loading experiment K

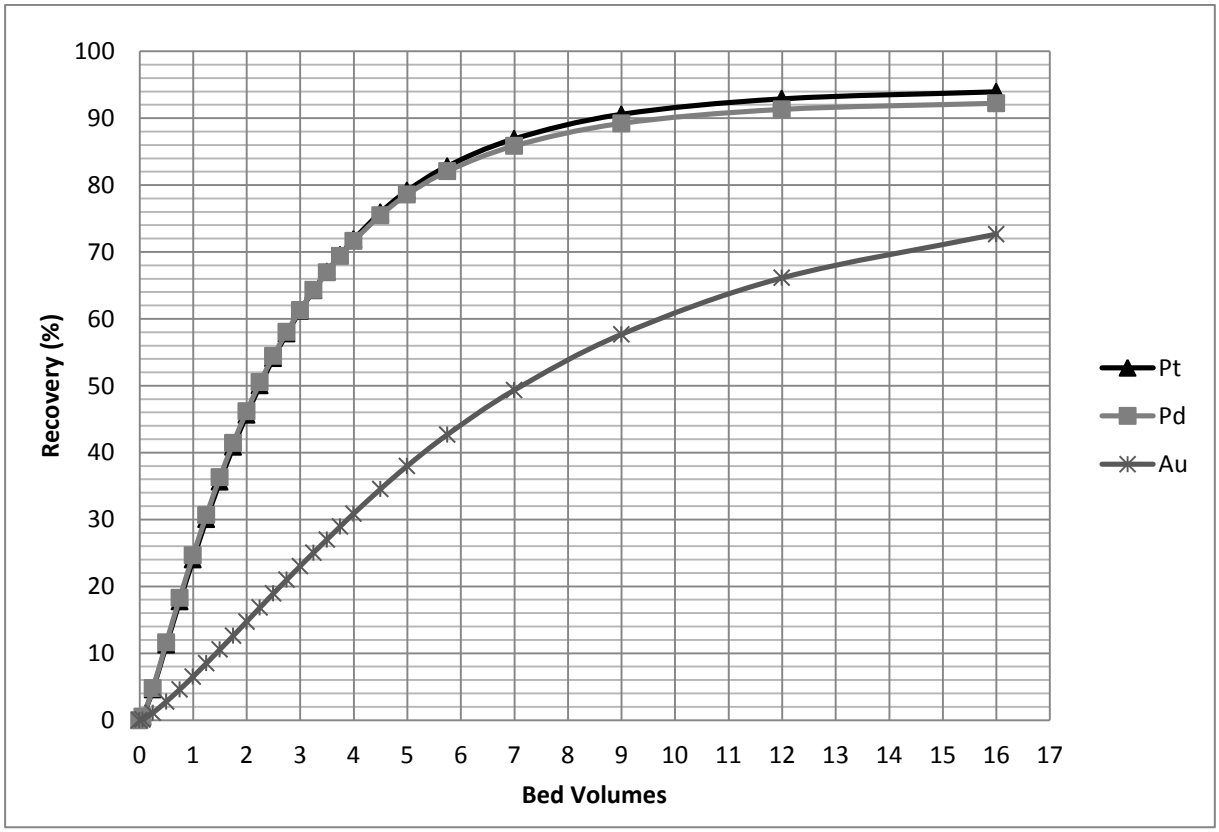
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	25

Elution	
Temperature (°C)	120
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**120 L T1**	9.58	15.93	24.02
0.25	**120 L T2**	15.30	25.72	38.90
0.50	**120 L T3**	17.23	25.19	38.42
0.75	**120 L T4**	17.63	24.25	36.82
1.00	**120 L T5**	19.34	22.98	35.86
1.25	**120 L T6**	19.63	21.72	33.73
1.50	**120 L T7**	19.84	20.07	31.34
1.75	**120 L T8**	19.91	17.99	29.16
2.00	**120 L T9**	20.65	16.98	26.52
2.25	**120 L T10**	20.26	15.37	24.54
2.50	**120 L T11**	20.09	13.87	22.57
2.75	**120 L T12**	19.65	12.69	20.40
3.00	**120 L T13**	19.70	11.69	18.77
3.25	**120 L T14**	19.06	10.37	17.03
3.50	**120 L T15**	18.93	9.41	15.06
3.75	**120 L T16**	18.90	8.75	14.04
4.00	**120 L T17**	18.14	7.84	12.88
4.50	**120 L T18**	17.25	6.39	10.45
5.00	**120 L T19**	16.03	5.12	8.37
5.75	**120 L T20**	14.13	3.48	5.83
7.00	**120 L T21**	11.57	2.14	3.66
9.00	**120 L T22**	8.52	0.98	1.66
12.00	**120 L T23**	5.06	0.31	0.57
16.00	**120 L T24**	2.83	0.11	0.19



Volume	BV	Pd (mg)	Recovery (%)	Pt	Recovery (%)	Au	Recovery (%)
0.00	0.00	0.04	0.00	0.06	0.00	0.02	0.00
4.80	0.06	0.32	0.52	0.48	0.50	0.19	0.12
20.00	0.25	0.51	4.78	0.77	4.62	0.33	1.10
40.00	0.50	0.49	11.64	0.75	11.28	0.35	2.78
60.00	0.75	0.47	18.31	0.73	17.77	0.37	4.59
80.00	1.00	0.45	24.67	0.70	24.04	0.39	6.51
100.00	1.25	0.42	30.70	0.65	30.04	0.39	8.53
120.00	1.50	0.38	36.33	0.61	35.65	0.40	10.57
140.00	1.75	0.35	41.46	0.56	40.86	0.41	12.63
160.00	2.00	0.32	46.17	0.51	45.66	0.41	14.73
180.00	2.25	0.29	50.53	0.47	50.06	0.40	16.85
200.00	2.50	0.27	54.47	0.43	54.12	0.40	18.94
220.00	2.75	0.24	58.05	0.39	57.83	0.39	21.00
240.00	3.00	0.22	61.34	0.36	61.20	0.39	23.04
260.00	3.25	0.20	64.31	0.32	64.29	0.38	25.05
280.00	3.50	0.18	66.97	0.29	67.06	0.38	27.02
300.00	3.75	0.17	69.42	0.27	69.57	0.37	28.98
320.00	4.00	0.28	71.66	0.47	71.89	0.71	30.90
360.00	4.50	0.23	75.49	0.38	75.91	0.67	34.56
400.00	5.00	0.26	78.60	0.43	79.15	0.90	38.01
460.00	5.75	0.28	82.08	0.47	82.83	1.29	42.70
560.00	7.00	0.25	85.86	0.43	86.92	1.61	49.36
720.00	9.00	0.16	89.23	0.27	90.58	1.63	57.68
960.00	12.00	0.07	91.32	0.12	92.89	1.26	66.13
1280.00	16.00		92.23		93.95		72.67
Sum (mg)		**6.78**		**10.78**		**12.76**	



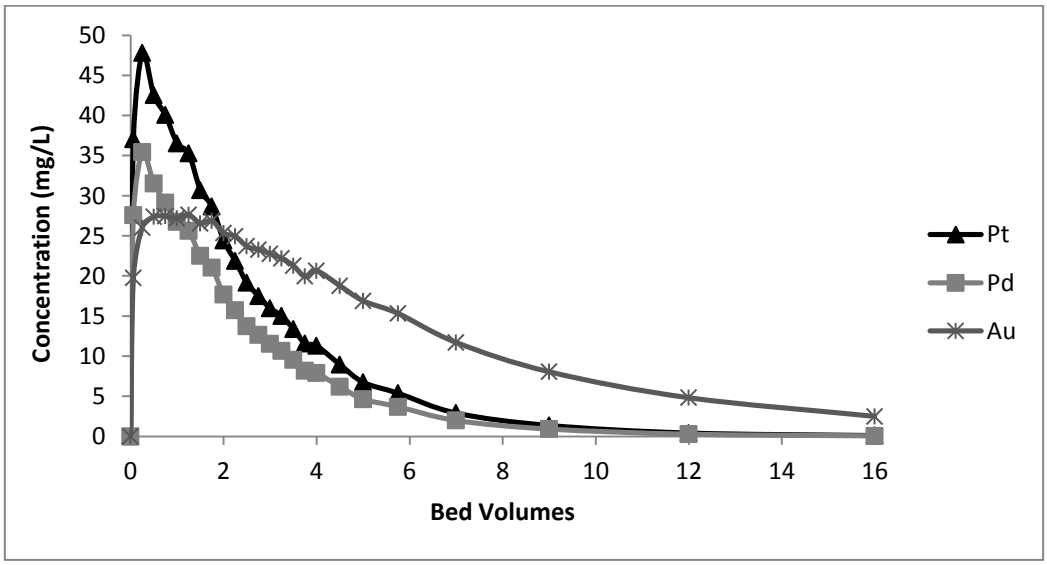
Elution experiment T5

From carbon loading experiment J

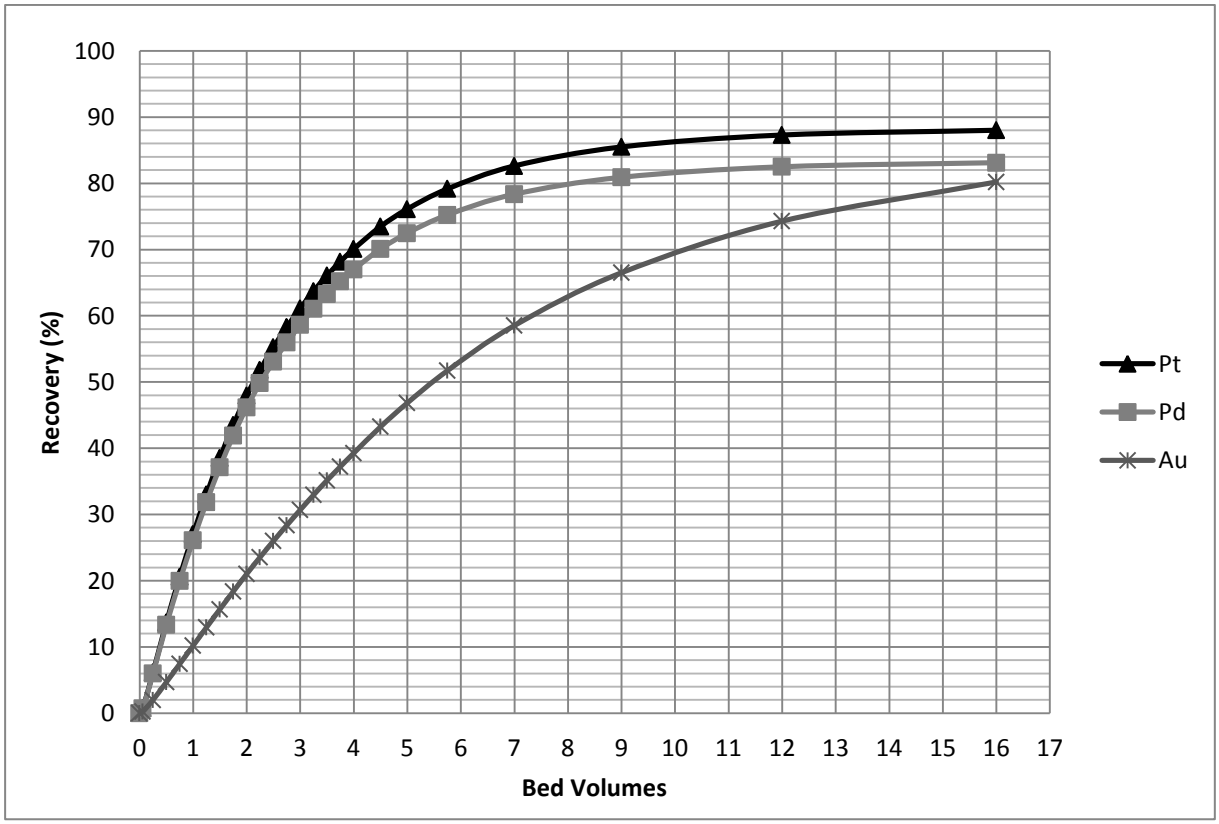
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	25

Elution	
Temperature (°C)	130
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**130 L T1**	19.76	27.58	37.02
0.25	**130 L T2**	26.04	35.45	47.79
0.50	**130 L T3**	27.38	31.51	42.53
0.75	**130 L T4**	27.44	29.15	40.05
1.00	**130 L T5**	27.19	26.73	36.53
1.25	**130 L T6**	27.62	25.62	35.27
1.50	**130 L T7**	26.56	22.50	30.70
1.75	**130 L T8**	26.87	21.02	28.65
2.00	**130 L T9**	25.34	17.67	24.42
2.25	**130 L T10**	24.95	15.72	21.87
2.50	**130 L T11**	23.69	13.73	19.15
2.75	**130 L T12**	23.29	12.66	17.49
3.00	**130 L T13**	22.77	11.54	15.97
3.25	**130 L T14**	22.18	10.66	15.03
3.50	**130 L T15**	21.28	9.54	13.37
3.75	**130 L T16**	19.94	8.20	11.59
4.00	**130 L T17**	20.64	7.90	11.29
4.50	**130 L T18**	18.78	6.21	8.95
5.00	**130 L T19**	16.90	4.66	6.75
5.75	**130 L T20**	15.33	3.70	5.39
7.00	**130 L T21**	11.71	1.99	2.91
9.00	**130 L T22**	8.06	0.92	1.37
12.00	**130 L T23**	4.83	0.28	0.42
16.00	**130 L T24**	2.50	0.07	0.11



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.07	0.00	0.09	0.00	0.05	0.00
4.80	0.06	0.48	0.73	0.64	0.74	0.35	0.24
20.00	0.25	0.67	5.98	0.90	6.14	0.53	1.99
40.00	0.50	0.61	13.34	0.83	13.70	0.55	4.69
60.00	0.75	0.56	19.99	0.77	20.61	0.55	7.45
80.00	1.00	0.52	26.13	0.72	27.01	0.55	10.20
100.00	1.25	0.48	31.87	0.66	33.02	0.54	12.97
120.00	1.50	0.44	37.16	0.59	38.54	0.53	15.70
140.00	1.75	0.39	41.93	0.53	43.51	0.52	18.39
160.00	2.00	0.33	46.18	0.46	47.95	0.50	21.02
180.00	2.25	0.29	49.85	0.41	51.82	0.49	23.56
200.00	2.50	0.26	53.08	0.37	55.26	0.47	26.01
220.00	2.75	0.24	55.97	0.33	58.32	0.46	28.38
240.00	3.00	0.22	58.63	0.31	61.12	0.45	30.70
260.00	3.25	0.20	61.07	0.28	63.72	0.43	32.96
280.00	3.50	0.18	63.29	0.25	66.09	0.41	35.15
300.00	3.75	0.16	65.23	0.23	68.18	0.41	37.23
320.00	4.00	0.28	67.00	0.40	70.10	0.79	39.28
360.00	4.50	0.22	70.10	0.31	73.49	0.71	43.25
400.00	5.00	0.25	72.48	0.36	76.11	0.97	46.85
460.00	5.75	0.28	75.23	0.41	79.16	1.35	51.72
560.00	7.00	0.23	78.36	0.34	82.63	1.58	58.53
720.00	9.00	0.14	80.91	0.22	85.50	1.55	66.50
960.00	12.00	0.06	82.50	0.09	87.30	1.17	74.29
1280.00	16.00		83.12		88.01		80.20
Sum (mg)		**7.52**		**10.43**		**14.74**	



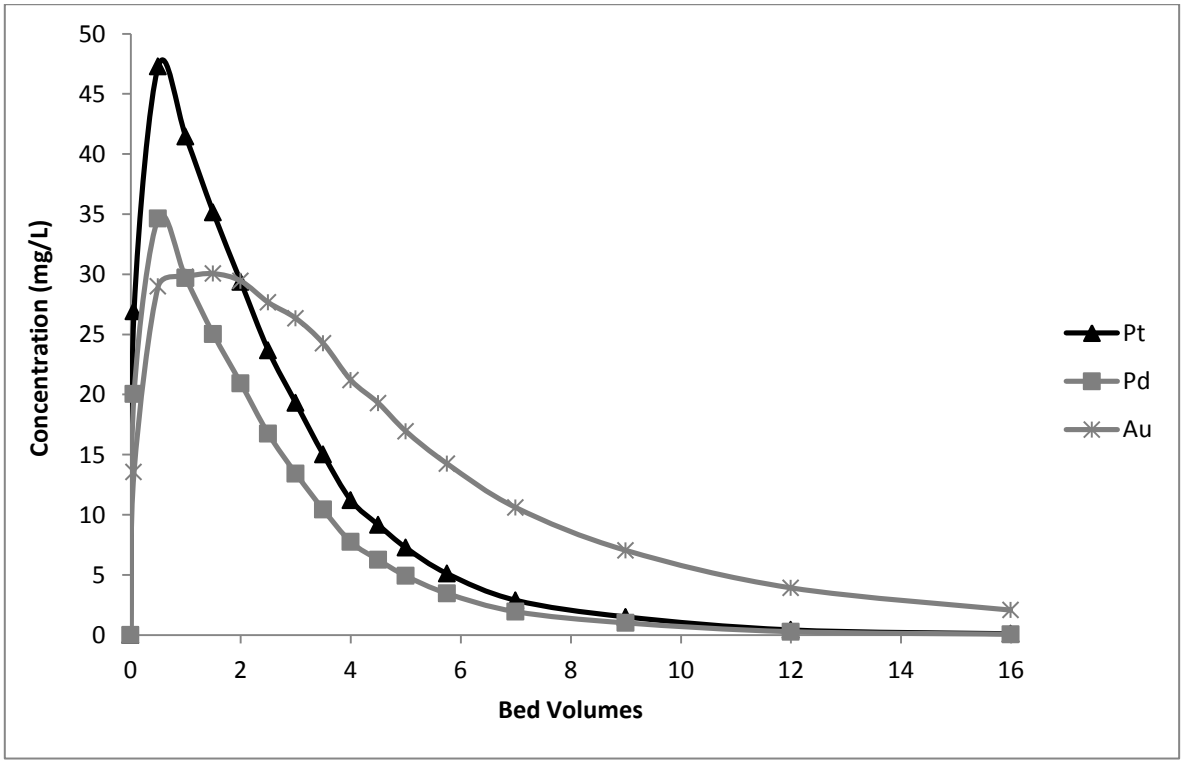
Elution experiment T6

From carbon loading experiment K

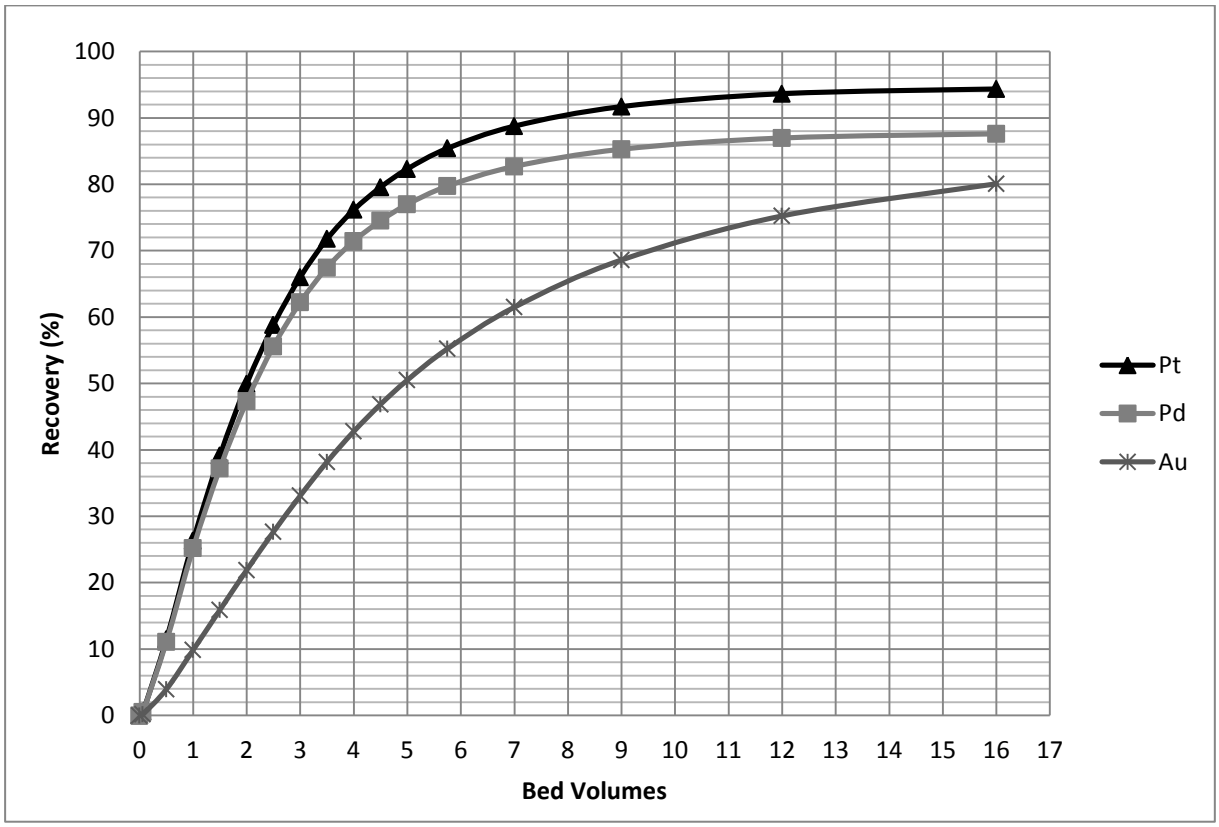
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	25

Elution	
Temperature (°C)	130
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**130 LR 1T**	13.57	20.04	26.92
0.50	**130 LR 3T**	29.00	34.64	47.28
1.00	**130 LR 5T**	29.79	29.68	41.46
1.50	**130 LR 7T**	30.05	25.03	35.14
2.00	**130 LR 9T**	29.44	20.94	29.38
2.50	**130 LR 11T**	27.66	16.74	23.68
3.00	**130 LR 13T**	26.34	13.43	19.30
3.50	**130 LR 15T**	24.25	10.43	15.01
4.00	**130 LR 17T**	21.20	7.74	11.22
4.50	**130 LR 18T**	19.29	6.25	9.16
5.00	**130 LR 19T**	16.95	4.92	7.27
5.75	**130 LR 20T**	14.25	3.46	5.11
7.00	**130 LR 21T**	10.60	1.94	2.89
9.00	**130 LR 22T**	7.04	1.01	1.51
12.00	**130 LR 23T**	3.92	0.28	0.42
16.00	**130 LR 24T**	2.07	0.07	0.11



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.02	0.00	0.02	0.00	0.01	0.00
1.80	0.06	0.36	0.20	0.49	0.20	0.28	0.06
15.00	0.50	0.48	4.16	0.67	4.30	0.44	1.48
30.00	1.00	0.41	9.45	0.57	9.87	0.45	3.70
45.00	1.50	0.34	13.96	0.48	14.68	0.45	5.96
60.00	2.00	0.28	17.74	0.40	18.73	0.43	8.21
75.00	2.50	0.23	20.85	0.32	22.06	0.41	10.37
90.00	3.00	0.18	23.33	0.26	24.75	0.38	12.41
105.00	3.50	0.14	25.29	0.20	26.91	0.34	14.32
120.00	4.00	0.10	26.79	0.15	28.55	0.30	16.04
135.00	4.50	0.08	27.94	0.12	29.83	0.27	17.57
150.00	5.00	0.09	28.86	0.14	30.86	0.35	18.94
172.50	5.75	0.10	29.90	0.15	32.03	0.47	20.71
210.00	7.00	0.09	31.01	0.13	33.28	0.53	23.06
270.00	9.00	0.06	31.98	0.09	34.39	0.49	25.73
360.00	12.00	0.02	32.62	0.03	35.12	0.36	28.21
480.00	16.00		32.85		35.38		30.03
Sum (mg)		**2.99**		**4.23**		**5.96**	



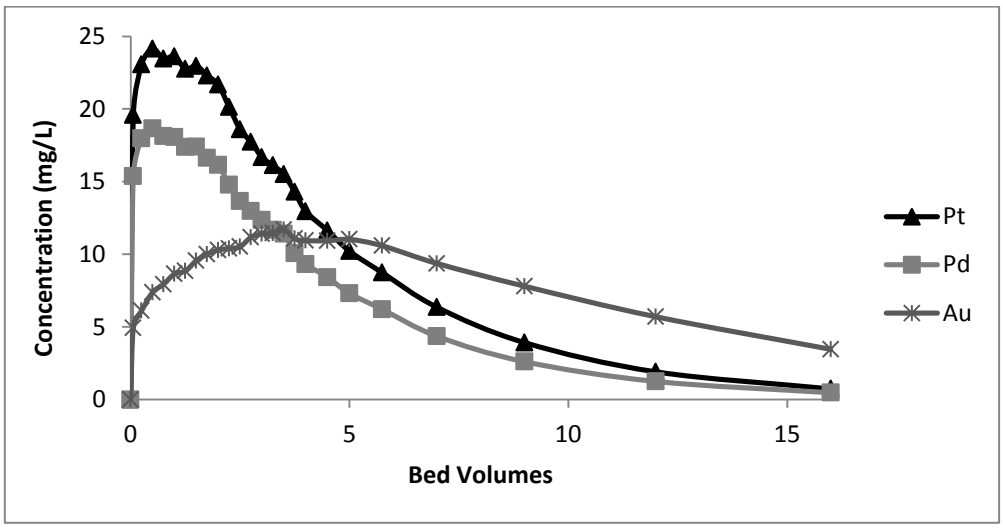
Elution experiment T7

From carbon loading experiment J

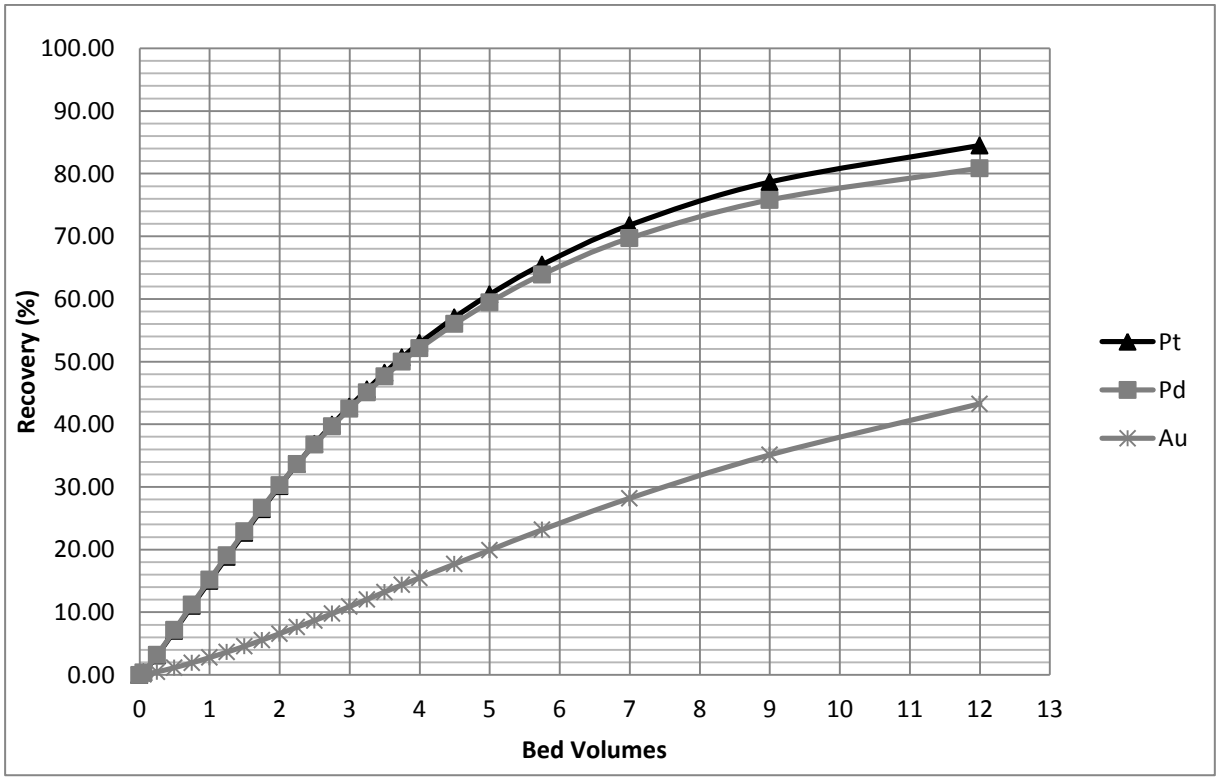
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	80

Elution	
Temperature (°C)	100
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**100 H T1**	4.92	15.38	19.59
0.25	**100 H T2**	6.12	17.98	23.07
0.50	**100 H T3**	7.37	18.66	24.15
0.75	**100 H T4**	7.93	18.12	23.45
1.00	**100 H T5**	8.65	18.07	23.62
1.25	**100 H T6**	8.85	17.38	22.75
1.50	**100 H T7**	9.56	17.39	22.96
1.75	**100 H T8**	10.00	16.63	22.30
2.00	**100 H T9**	10.29	16.14	21.67
2.25	**100 H T10**	10.39	14.77	20.13
2.50	**100 H T11**	10.52	13.66	18.59
2.75	**100 H T12**	11.17	12.96	17.72
3.00	**100 H T13**	11.40	12.36	16.67
3.25	**100 H T14**	11.44	11.66	16.11
3.50	**100 H T15**	11.70	11.41	15.50
3.75	**100 H T16**	11.07	10.06	14.28
4.00	**100 H T17**	10.94	9.32	12.95
4.50	**100 H T18**	10.93	8.40	11.62
5.00	**100 H T19**	11.02	7.31	10.21
5.75	**100 H T20**	10.58	6.20	8.73
7.00	**100 H T21**	9.37	4.35	6.35
9.00	**100 H T22**	7.80	2.60	3.92
12.00	**100 H T23**	5.70	1.24	1.91
16.00	**100 H T24**	3.46	0.47	0.73



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.05	0.00	0.01	0.00
4.80	0.06	0.25	0.41	0.32	0.39	0.08	0.06
20.00	0.25	0.37	3.19	0.47	3.11	0.13	0.48
40.00	0.50	0.37	7.21	0.48	7.06	0.15	1.16
60.00	0.75	0.36	11.25	0.47	11.04	0.17	1.93
80.00	1.00	0.35	15.22	0.46	14.98	0.17	2.77
100.00	1.25	0.35	19.11	0.46	18.86	0.18	3.65
120.00	1.50	0.34	22.93	0.45	22.69	0.20	4.58
140.00	1.75	0.33	26.66	0.44	26.47	0.20	5.56
160.00	2.00	0.31	30.26	0.42	30.15	0.21	6.59
180.00	2.25	0.28	33.65	0.39	33.65	0.21	7.63
200.00	2.50	0.27	36.77	0.36	36.89	0.22	8.68
220.00	2.75	0.25	39.70	0.34	39.93	0.23	9.78
240.00	3.00	0.24	42.47	0.33	42.81	0.23	10.91
260.00	3.25	0.23	45.11	0.32	45.55	0.23	12.06
280.00	3.50	0.21	47.64	0.30	48.20	0.23	13.23
300.00	3.75	0.19	50.00	0.27	50.69	0.22	14.38
320.00	4.00	0.35	52.13	0.49	52.97	0.44	15.49
360.00	4.50	0.31	56.02	0.44	57.08	0.44	17.69
400.00	5.00	0.41	59.47	0.57	60.73	0.65	19.91
460.00	5.75	0.53	63.92	0.75	65.49	1.00	23.17
560.00	7.00	0.56	69.71	0.82	71.79	1.37	28.20
720.00	9.00	0.46	75.82	0.70	78.67	1.62	35.12
960.00	12.00	0.27	80.88	0.42	84.51	1.46	43.28
1280.00	16.00		83.88		88.04		50.66
Sum (mg)		**7.37**		**10.10**		**8.59**	



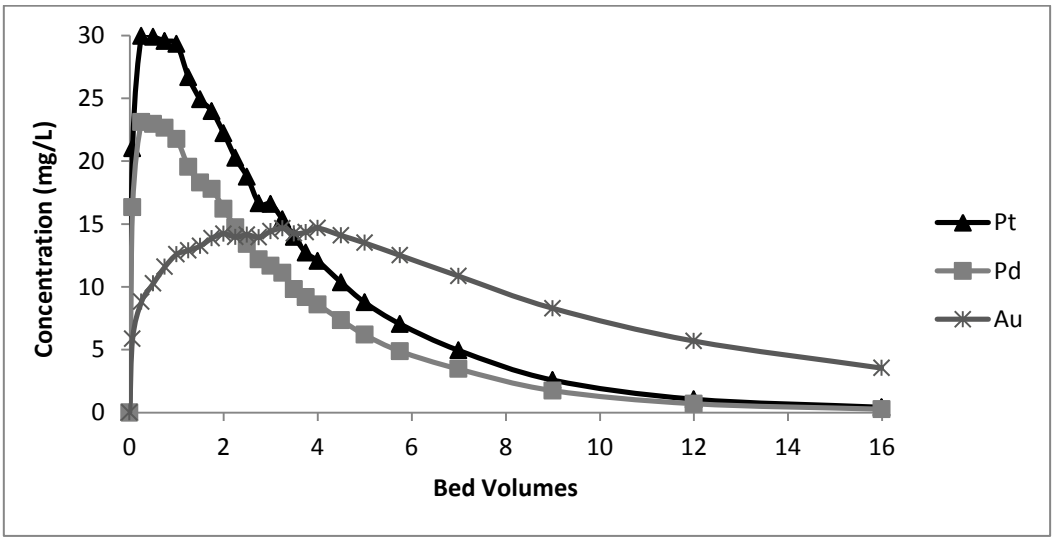
Elution experiment T8

From carbon loading experiment J

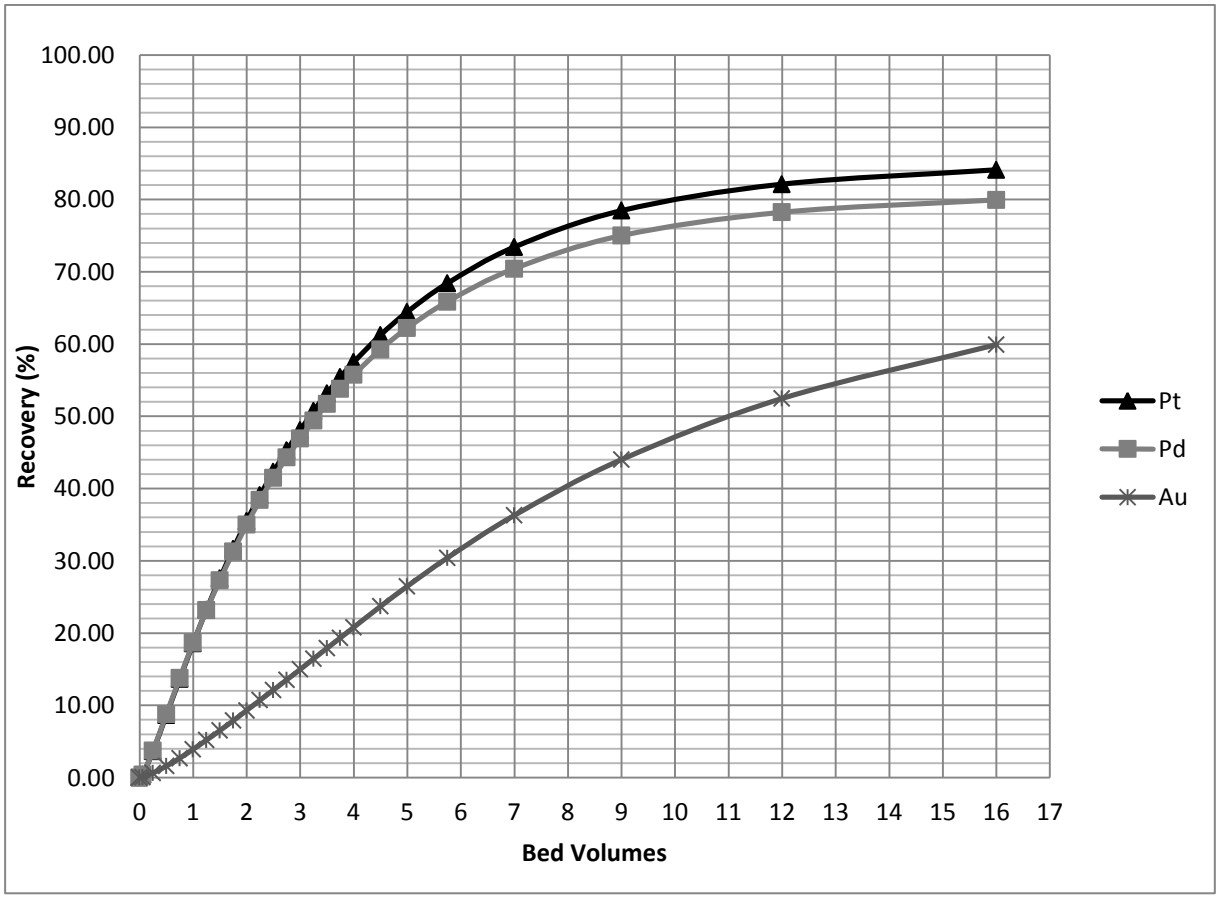
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	80

Elution	
Temperature (°C)	110
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**110 H T1**	5.86	16.34	21.02
0.25	**110 H T2**	8.81	23.11	29.96
0.50	**110 H T3**	10.26	22.94	29.87
0.75	**110 H T4**	11.60	22.63	29.55
1.00	**110 H T5**	12.59	21.75	29.31
1.25	**110 H T6**	12.89	19.53	26.66
1.50	**110 H T7**	13.25	18.29	24.92
1.75	**110 H T8**	13.87	17.77	23.97
2.00	**110 H T9**	14.22	16.21	22.21
2.25	**110 H T10**	13.95	14.73	20.24
2.50	**110 H T11**	14.14	13.39	18.74
2.75	**110 H T12**	13.94	12.18	16.63
3.00	**110 H T13**	14.42	11.66	16.58
3.25	**110 H T14**	14.66	11.11	15.36
3.50	**110 H T15**	14.25	9.81	13.96
3.75	**110 H T16**	14.34	9.18	12.70
4.00	**110 H T17**	14.67	8.60	12.06
4.50	**110 H T18**	14.08	7.34	10.34
5.00	**110 H T19**	13.49	6.18	8.76
5.75	**110 H T20**	12.50	4.88	7.04
7.00	**110 H T21**	10.85	3.46	4.94
9.00	**110 H T22**	8.29	1.75	2.58
12.00	**110 H T23**	5.69	0.71	1.06
16.00	**110 H T24**	3.54	0.27	0.42



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.05	0.00	0.01	0.00
4.80	0.06	0.30	0.43	0.39	0.42	0.11	0.07
20.00	0.25	0.46	3.72	0.60	3.66	0.19	0.63
40.00	0.50	0.46	8.78	0.59	8.67	0.22	1.59
60.00	0.75	0.44	13.78	0.59	13.64	0.24	2.70
80.00	1.00	0.41	18.65	0.56	18.57	0.25	3.91
100.00	1.25	0.38	23.18	0.52	23.25	0.26	5.20
120.00	1.50	0.36	27.33	0.49	27.57	0.27	6.52
140.00	1.75	0.34	31.29	0.46	31.66	0.28	7.88
160.00	2.00	0.31	35.02	0.42	35.52	0.28	9.30
180.00	2.25	0.28	38.42	0.39	39.08	0.28	10.72
200.00	2.50	0.26	41.50	0.35	42.34	0.28	12.14
220.00	2.75	0.24	44.31	0.33	45.30	0.28	13.55
240.00	3.00	0.23	46.93	0.32	48.08	0.29	14.98
260.00	3.25	0.21	49.43	0.29	50.75	0.29	16.45
280.00	3.50	0.19	51.72	0.27	53.20	0.29	17.90
300.00	3.75	0.18	53.81	0.25	55.44	0.29	19.34
320.00	4.00	0.32	55.76	0.45	57.51	0.58	20.81
360.00	4.50	0.27	59.26	0.38	61.26	0.55	23.70
400.00	5.00	0.33	62.23	0.47	64.45	0.78	26.48
460.00	5.75	0.42	65.87	0.60	68.42	1.17	30.41
560.00	7.00	0.42	70.44	0.60	73.43	1.53	36.30
720.00	9.00	0.29	75.01	0.44	78.47	1.68	44.02
960.00	12.00	0.16	78.24	0.24	82.13	1.48	52.47
1280.00	16.00		79.96		84.12		59.91
Sum (mg)		**7.13**		**9.81**		**10.41**	



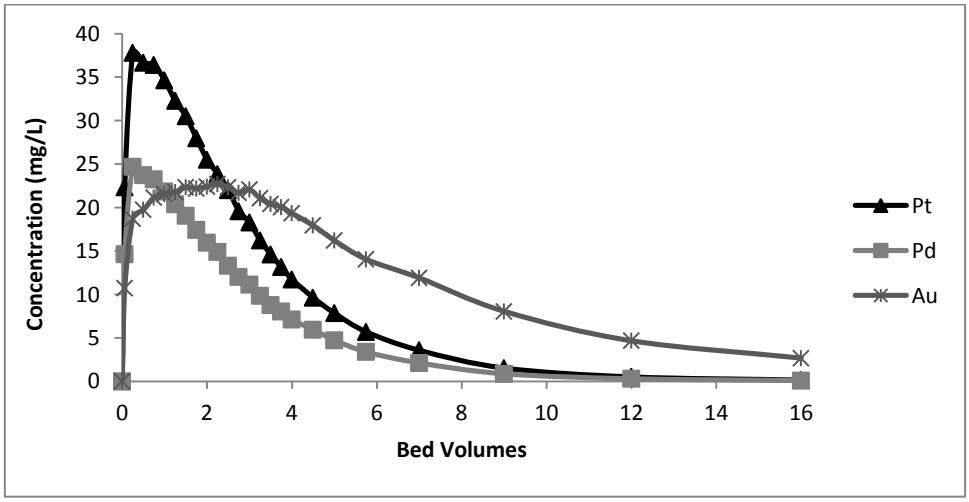
Elution experiment T9

From carbon loading experiment K

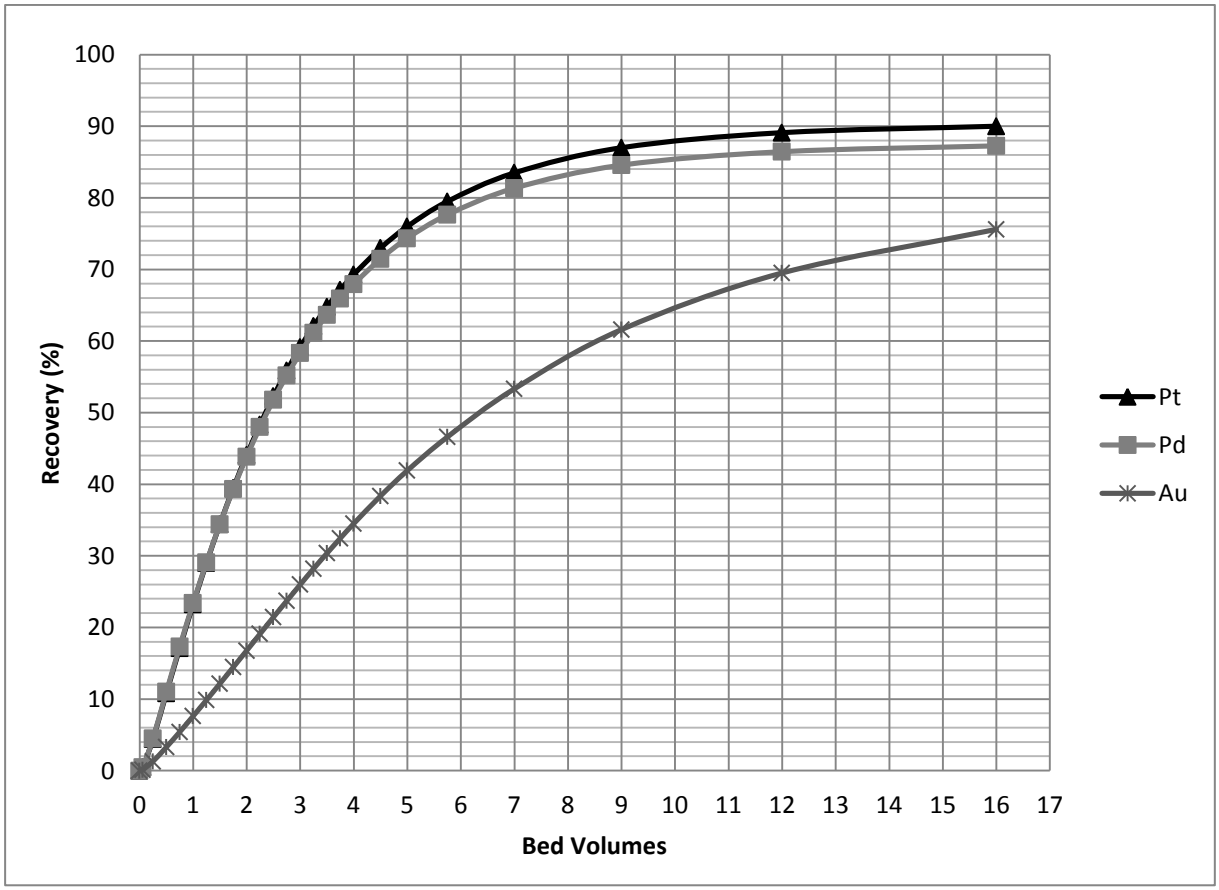
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	80

Elution	
Temperature (°C)	120
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**120 H T1**	10.73	14.63	22.32
0.25	**120 H T2**	18.73	24.67	37.80
0.50	**120 H T3**	19.73	23.71	36.67
0.75	**120 H T4**	21.16	23.23	36.40
1.00	**120 H T5**	21.55	21.86	34.62
1.25	**120 H T6**	21.79	20.36	32.28
1.50	**120 H T7**	22.34	19.04	30.50
1.75	**120 H T8**	22.18	17.43	27.96
2.00	**120 H T9**	22.41	15.94	25.51
2.25	**120 H T10**	22.71	14.87	23.85
2.50	**120 H T11**	22.31	13.31	22.00
2.75	**120 H T12**	21.69	12.00	19.58
3.00	**120 H T13**	22.06	11.14	18.29
3.25	**120 H T14**	21.06	9.84	16.22
3.50	**120 H T15**	20.42	8.77	14.59
3.75	**120 H T16**	20.06	8.03	13.15
4.00	**120 H T17**	19.33	7.11	11.73
4.50	**120 H T18**	17.93	5.95	9.63
5.00	**120 H T19**	16.21	4.74	7.84
5.75	**120 H T20**	14.04	3.39	5.70
7.00	**120 H T21**	11.90	2.12	3.57
9.00	**120 H T22**	8.05	0.87	1.53
12.00	**120 H T23**	4.67	0.29	0.51
16.00	**120 H T24**	2.67	0.09	0.15



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.04	0.00	0.05	0.00	0.03	0.00
4.80	0.06	0.30	0.47	0.46	0.46	0.22	0.13
20.00	0.25	0.48	4.50	0.74	4.40	0.38	1.29
40.00	0.50	0.47	11.02	0.73	10.82	0.41	3.29
60.00	0.75	0.45	17.34	0.71	17.12	0.43	5.40
80.00	1.00	0.42	23.42	0.67	23.24	0.43	7.62
100.00	1.25	0.39	29.11	0.63	29.01	0.44	9.86
120.00	1.50	0.36	34.42	0.58	34.42	0.45	12.15
140.00	1.75	0.33	39.34	0.53	39.46	0.45	14.46
160.00	2.00	0.31	43.83	0.49	44.07	0.45	16.77
180.00	2.25	0.28	47.99	0.46	48.33	0.45	19.10
200.00	2.50	0.25	51.78	0.42	52.28	0.44	21.44
220.00	2.75	0.23	55.20	0.38	55.86	0.44	23.72
240.00	3.00	0.21	58.31	0.35	59.13	0.43	25.98
260.00	3.25	0.19	61.14	0.31	62.10	0.41	28.22
280.00	3.50	0.17	63.65	0.28	64.76	0.40	30.37
300.00	3.75	0.15	65.91	0.25	67.15	0.39	32.47
320.00	4.00	0.26	67.95	0.43	69.29	0.75	34.51
360.00	4.50	0.21	71.47	0.35	72.98	0.68	38.37
400.00	5.00	0.24	74.35	0.41	75.99	0.91	41.90
460.00	5.75	0.28	77.64	0.46	79.49	1.30	46.61
560.00	7.00	0.24	81.34	0.41	83.48	1.60	53.33
720.00	9.00	0.14	84.56	0.24	87.00	1.53	61.60
960.00	12.00	0.06	86.44	0.10	89.10	1.17	69.51
1280.00	16.00		87.25		90.00		75.59
Sum (mg)		**6.41**		**10.34**		**13.41**	



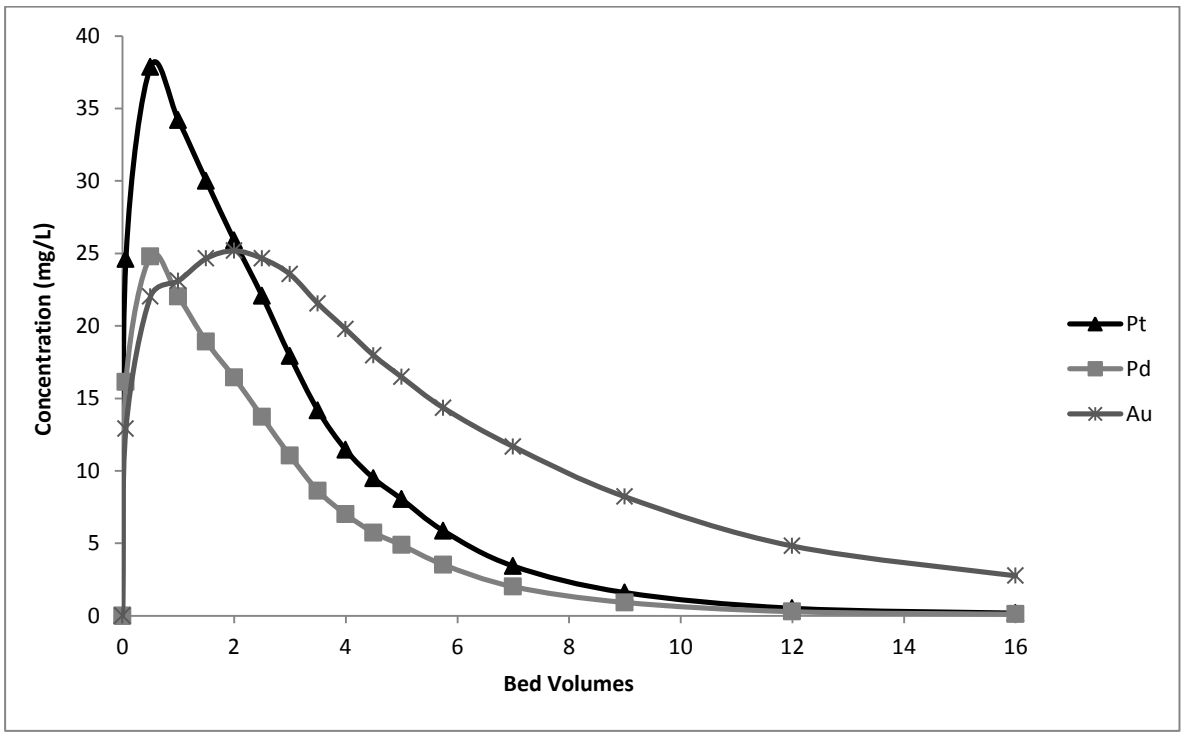
Elution experiment T10

From carbon loading experiment K

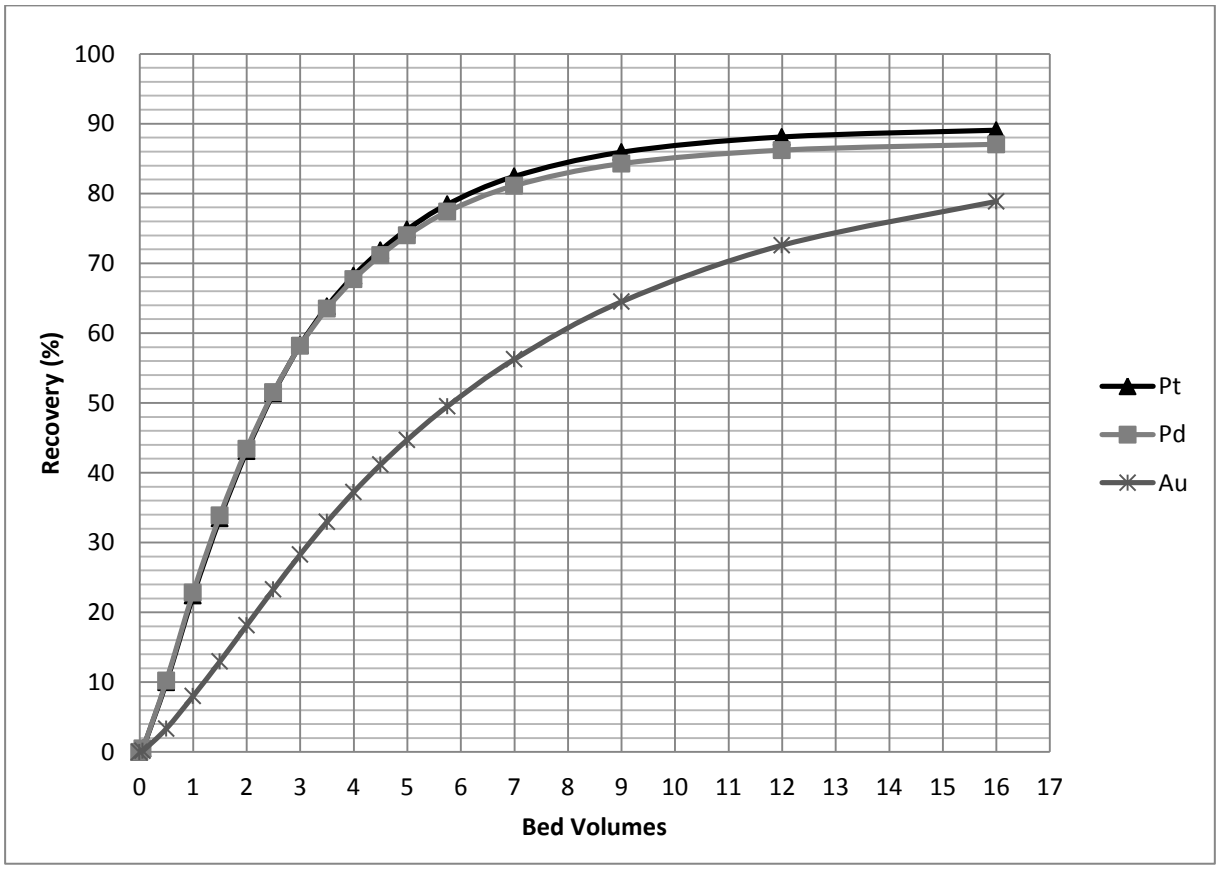
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	80

Elution	
Temperature (°C)	120
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**120 HR 1T**	12.90	16.12	24.60
0.50	**120 HR 3T**	22.02	24.79	37.86
1.00	**120 HR 5T**	23.10	22.02	34.19
1.50	**120 HR 7T**	24.65	18.91	30.00
2.00	**120 HR 9T**	25.18	16.44	25.90
2.50	**120 HR 11T**	24.65	13.72	22.07
3.00	**120 HR 13T**	23.56	11.04	17.91
3.50	**120 HR 15T**	21.54	8.63	14.17
4.00	**120 HR 17T**	19.77	7.00	11.44
4.50	**120 HR 18T**	17.96	5.73	9.48
5.00	**120 HR 19T**	16.47	4.87	8.05
5.75	**120 HR 20T**	14.34	3.52	5.86
7.00	**120 HR 21T**	11.67	2.01	3.43
9.00	**120 HR 22T**	8.21	0.92	1.60
12.00	**120 HR 23T**	4.81	0.28	0.51
16.00	**120 HR 24T**	2.76	0.11	0.18



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0	0.04	0.00	0.06	0.00	0.03	0.00
4.80	0.06	0.72	0.52	1.10	0.51	0.61	0.16
40.00	0.5	0.94	10.23	1.44	9.99	0.90	3.34
80.00	1	0.82	22.84	1.28	22.41	0.96	8.02
120.00	1.5	0.71	33.87	1.12	33.48	1.00	12.97
160.00	2	0.60	43.40	0.96	43.11	1.00	18.13
200.00	2.5	0.50	51.53	0.80	51.38	0.96	23.30
240.00	3	0.39	58.21	0.64	58.28	0.90	28.29
280.00	3.5	0.31	63.51	0.51	63.81	0.83	32.97
320.00	4	0.25	67.72	0.42	68.22	0.75	37.25
360.00	4.5	0.21	71.15	0.35	71.83	0.69	41.16
400.00	5	0.25	74.01	0.42	74.85	0.92	44.72
460.00	5.75	0.28	77.40	0.46	78.45	1.30	49.51
560.00	7	0.23	81.13	0.40	82.45	1.59	56.25
720.00	9	0.14	84.28	0.25	85.92	1.56	64.49
960.00	12	0.06	86.21	0.11	88.10	1.21	72.59
1280.00	16		87.05		89.06		78.87
Sum (mg)		**6.46**		**10.33**		**15.22**	



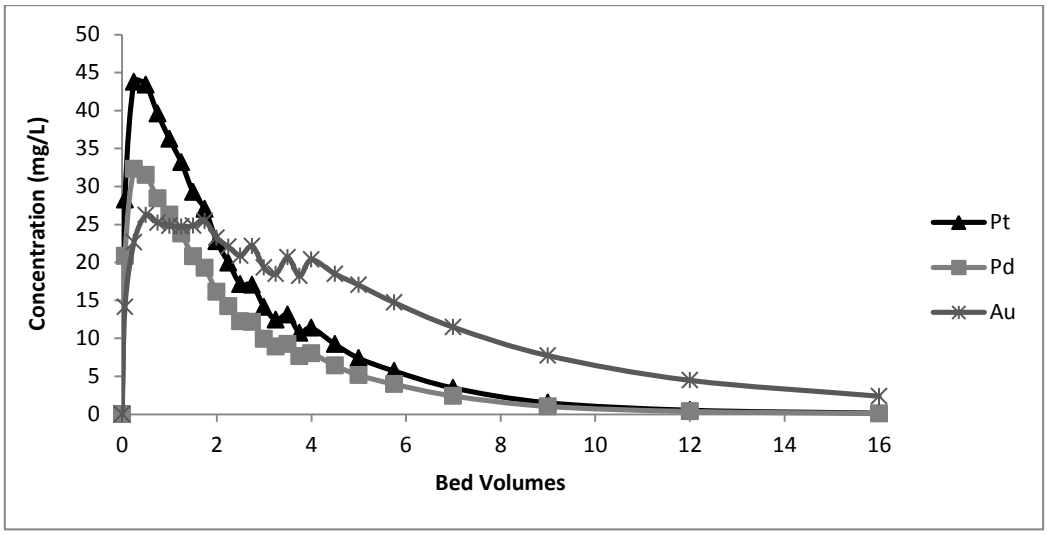
Elution experiment T11

From carbon loading experiment J

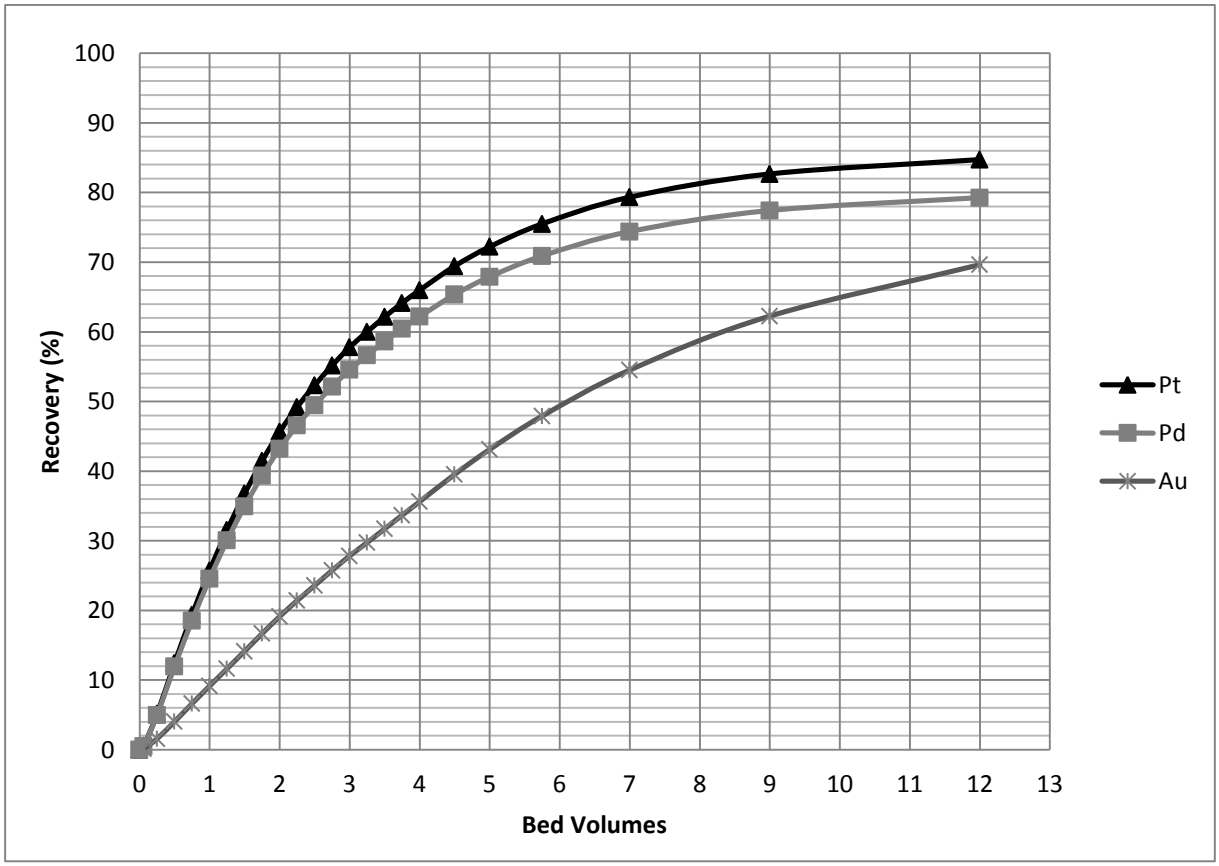
Pre-treatment step	
NaOH (%)	0.55
NaCN (%)	2
Volume (mL)	210
Stirred (min)	30
Activated Carbon (wet g)	56
Pre-treatment temperature (°C)	80

Elution	
Temperature (°C)	130
Bed Volume (mL)	80
Flow rate (BV/hr)	30.0

BV		Au	Pd	Pt
0.00		0	0	0
0.06	**130 H T1**	14.15	20.82	28.25
0.25	**130 H T2**	22.66	32.30	43.75
0.50	**130 H T3**	26.21	31.49	43.40
0.75	**130 H T4**	25.23	28.44	39.61
1.00	**130 H T5**	24.78	26.27	36.26
1.25	**130 H T6**	24.73	23.79	33.17
1.50	**130 H T7**	24.82	20.79	29.25
1.75	**130 H T8**	25.41	19.27	27.01
2.00	**130 H T9**	23.23	16.11	22.76
2.25	**130 H T10**	22.04	14.20	19.94
2.50	**130 H T11**	20.89	12.22	17.14
2.75	**130 H T12**	22.16	12.15	17.05
3.00	**130 H T13**	19.33	9.91	14.12
3.25	**130 H T14**	18.49	8.92	12.44
3.50	**130 H T15**	20.65	9.25	13.11
3.75	**130 H T16**	18.21	7.65	10.72
4.00	**130 H T17**	20.36	8.00	11.38
4.50	**130 H T18**	18.49	6.42	9.22
5.00	**130 H T19**	17.02	5.15	7.39
5.75	**130 H T20**	14.72	3.96	5.70
7.00	**130 H T21**	11.47	2.41	3.47
9.00	**130 H T22**	7.73	1.03	1.52
12.00	**130 H T23**	4.47	0.37	0.54
16.00	**130 H T24**	2.39	0.10	0.16



Volume	BV	Pd (mg)	Recovery (%)	Pt (mg)	Recovery (%)	Au (mg)	Recovery (%)
0.00	0.00	0.05	0.00	0.07	0.00	0.03	0.00
4.80	0.06	0.40	0.55	0.55	0.57	0.28	0.17
20.00	0.25	0.64	4.98	0.87	5.15	0.49	1.58
40.00	0.50	0.60	11.98	0.83	12.44	0.51	4.04
60.00	0.75	0.55	18.56	0.76	19.39	0.50	6.64
80.00	1.00	0.50	24.57	0.69	25.73	0.50	9.16
100.00	1.25	0.45	30.06	0.62	31.54	0.50	11.65
120.00	1.50	0.40	34.95	0.56	36.77	0.50	14.15
140.00	1.75	0.35	39.35	0.50	41.48	0.49	16.68
160.00	2.00	0.30	43.24	0.43	45.64	0.45	19.13
180.00	2.25	0.26	46.56	0.37	49.21	0.43	21.42
200.00	2.50	0.24	49.46	0.34	52.32	0.43	23.58
220.00	2.75	0.22	52.14	0.31	55.18	0.41	25.75
240.00	3.00	0.19	54.56	0.27	57.79	0.38	27.84
260.00	3.25	0.18	56.63	0.26	60.01	0.39	29.75
280.00	3.50	0.17	58.62	0.24	62.15	0.39	31.72
300.00	3.75	0.16	60.48	0.22	64.14	0.39	33.68
320.00	4.00	0.29	62.20	0.41	65.99	0.78	35.62
360.00	4.50	0.23	65.36	0.33	69.44	0.71	39.54
400.00	5.00	0.27	67.90	0.39	72.22	0.95	43.12
460.00	5.75	0.32	70.90	0.46	75.50	1.31	47.92
560.00	7.00	0.28	74.40	0.40	79.33	1.54	54.52
720.00	9.00	0.17	77.42	0.25	82.67	1.46	62.26
960.00	12.00	0.08	79.27	0.11	84.73	1.10	69.64
1280.00	16.00		80.11		85.66		75.17
Sum (mg)		**7.22**		**10.13**		**13.82**	



Appendix C

Mathematical modelling

User Defined Functions (UDFs) for Pt and Na source terms (C++ programming language)

Model example for pre-treatment concentrations of ≥ 2% NaCN

```
/*Model source terms for experiment P*/
#include"udf.h"

#define s 3.4e-6                                        /*define constants*/
#define f 2e-6                                          /*define Na rate constant*/
#define BATH_ID            /*ID of the fluid zone as in the boundary condition panel*/

static int last_ts = -1;                /* Global variable. Time step is never >0 */


DEFINE_ADJUST(Carbon_loading,d)   /*Adjustment of carbon loading as elution progress*/
{
  Thread *t;
  cell_t c;
  real time;

  int curr_ts;     /*method to only adjust on the first iteration of every time step*/
  curr_ts = N_TIME;

  t = Lookup_Thread(d,  BATH_ID);

  time = CURRENT_TIME;

  if (last_ts != curr_ts)
  {
   last_ts = curr_ts;
       begin_c_loop(c,t)
   {
               C_UDMI(c,t,1) = C_UDMI(c,t,1)*(1-s*(pow(2.718,-
540*C_YI(c,t,1)))*(19*(pow(C_UDMI(c,t,2),-0.29))-40))+(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));            /*adjustment of loading: Qt = Qt-1 – Ptsource*/
         C_UDMI(c,t,2) = C_UDMI(c,t,2)-f;                 /*adjustment of Na loading*/

        if (C_UDMI(c,t,1) > 0.00000001)     /*tjek amount of Pt left*/
              C_UDMI(c,t,3) = s*(pow(2.718,-540*C_YI(c,t,1)))*(C_UDMI(c,t,1)/(6.49e-
10*1000*1000))*(19*(pow(C_UDMI(c,t,2),-0.29))-40)-(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));                          /*Pt source term in kg/m3s*/
       else
              C_UDMI(c,t,3) = 0;          /*source term is 0 if carbon loading is 0*/

       if (C_UDMI(c,t,2) > 0.0000150)                                    /*Na source*/
              C_UDMI(c,t,4) = f/(6.49e-10*1000*1000);
       else
              C_UDMI(c,t,4) = 0;

       if (C_UDMI(c,t,2) > 0.0000150)
              C_UDMI(c,t,2)=C_UDMI(c,t,2);
       else
```

```
              C_UDMI(c,t,2)=0.0000150;

         }
        end_c_loop(c,t)
  }
}

DEFINE_SOURCE(platinum_source,c,t,dS,eqn)                              /*source terms*/
{
return C_UDMI(c,t,3);
}

DEFINE_SOURCE(Na_source,c,t,dS,eqn)
{
return C_UDMI(c,t,4);
}

/*define the initial carbon loading by setting a value to each cell*/
DEFINE_INIT(CUDMI,d)
{
  Thread *t;
  cell_t c;

  t = Lookup_Thread(d,  BATH_ID);

    begin_c_loop(c,t)
       {
              C_UDMI(c,t,1)=0.000202;                 /*Pt = 5.09 mg for 8 g AC. 25252
CELLS = 5.09/25252 = 0.000202 mg/cell*/
         C_UDMI(c,t,2)=0.00302;                        /*Na = 72 mg for 25252 cells*/
       }
     end_c_loop(c,t)

}
/*end*/
```

Model example for pre-treatment concentrations of 1% NaCN

```
/*Model source terms for experiment V*/
#include"udf.h"

#define s 3.4e-6                                        /*define constants*/
#define f 2e-6                                          /*define Na rate constant*/
#define BATH_ID            /*ID of the fluid zone as in the boundary condition panel*/

static int last_ts = -1;                /* Global variable. Time step is never >0 */


DEFINE_ADJUST(Carbon_loading,d)   /*Adjustment of carbon loading as elution progress*/
{
  Thread *t;
  cell_t c;
  real time;

  int curr_ts;     /*method to only adjust on the first iteration of every time step*/
  curr_ts = N_TIME;

  t = Lookup_Thread(d,  BATH_ID);

  time = CURRENT_TIME;

  if (last_ts != curr_ts)
  {
   last_ts = curr_ts;
       begin_c_loop(c,t)
   {
              C_UDMI(c,t,1) = C_UDMI(c,t,1)*(1-s*(pow(2.718,-
540*C_YI(c,t,1)))*(0.65*(19*(pow(C_UDMI(c,t,2),-0.29))-40))+(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));            /*adjustment of loading: Qt = Qt-1 – Ptsource*/
         C_UDMI(c,t,2) = C_UDMI(c,t,2)-f;                 /*adjustment of Na loading*/

        if (C_UDMI(c,t,1) > 0.00000001)     /*tjek amount of Pt left*/
              C_UDMI(c,t,3) = s*(pow(2.718,-540*C_YI(c,t,1)))*(C_UDMI(c,t,1)/(6.49e-
10*1000*1000))*(0.65*(19*(pow(C_UDMI(c,t,2),-0.29))-40)-(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));                          /*Pt source term in kg/m3s*/
       else
              C_UDMI(c,t,3) = 0;          /*source term is 0 if carbon loading is 0*/

       if (C_UDMI(c,t,2) > 0.0000150)                                    /*Na source*/
              C_UDMI(c,t,4) = f/(6.49e-10*1000*1000);
       else
              C_UDMI(c,t,4) = 0;

       if (C_UDMI(c,t,2) > 0.0000150)
              C_UDMI(c,t,2)=C_UDMI(c,t,2);
       else
              C_UDMI(c,t,2)=0.0000150;

        }
       end_c_loop(c,t)
  }
}

DEFINE_SOURCE(platinum_source,c,t,dS,eqn)                          /*source terms*/
{
return C_UDMI(c,t,3);
}

DEFINE_SOURCE(Na_source,c,t,dS,eqn)
```

```
{
return C_UDMI(c,t,4);
}

/*define the initial carbon loading by setting a value to each cell*/
DEFINE_INIT(CUDMI,d)
{
  Thread *t;
  cell_t c;

  t = Lookup_Thread(d,  BATH_ID);

    begin_c_loop(c,t)
       {
              C_UDMI(c,t,1)=0.000168;                 /*Pt = 4.3 mg for 8 g AC. 25252
CELLS = 4.3/25252 = 0.000168 mg/cell*/
         C_UDMI(c,t,2)=0.0027;                         /*Na = 68 mg for 25252 cells*/
       }
     end_c_loop(c,t)

}
/*end*/
```

Model example for pre-treatment concentrations of 0% NaCN

```
/*Model source terms for experiment U*/
#include"udf.h"

#define s 3.4e-6                                        /*define constants*/
#define f 2e-6                                          /*define Na rate constant*/
#define BATH_ID            /*ID of the fluid zone as in the boundary condition panel*/

static int last_ts = -1;                /* Global variable. Time step is never >0 */


DEFINE_ADJUST(Carbon_loading,d)   /*Adjustment of carbon loading as elution progress*/
{
  Thread *t;
  cell_t c;
  real time;

  int curr_ts;     /*method to only adjust on the first iteration of every time step*/
  curr_ts = N_TIME;

  t = Lookup_Thread(d,  BATH_ID);

  time = CURRENT_TIME;

  if (last_ts != curr_ts)
  {
   last_ts = curr_ts;
       begin_c_loop(c,t)
   {
               C_UDMI(c,t,1) = C_UDMI(c,t,1)*(1-s*(pow(2.718,-
540*C_YI(c,t,1)))*(0.4*(19*(pow(C_UDMI(c,t,2),-0.29))-40))+(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));            /*adjustment of loading: Qt = Qt-1 – Ptsource*/
         C_UDMI(c,t,2) = C_UDMI(c,t,2)-f;                 /*adjustment of Na loading*/

        if (C_UDMI(c,t,1) > 0.00000001)     /*tjek amount of Pt left*/
              C_UDMI(c,t,3) = s*(pow(2.718,-540*C_YI(c,t,1)))*(C_UDMI(c,t,1)/(6.49e-
10*1000*1000))*(0.4*(19*(pow(C_UDMI(c,t,2),-0.29))-40)-(s*(pow(2.718,-
540*C_YI(c,t,1)))*C_YI(c,t,0));                          /*Pt source term in kg/m3s*/
       else
              C_UDMI(c,t,3) = 0;          /*source term is 0 if carbon loading is 0*/

       if (C_UDMI(c,t,2) > 0.0000150)                                    /*Na source*/
              C_UDMI(c,t,4) = f/(6.49e-10*1000*1000);
       else
              C_UDMI(c,t,4) = 0;

       if (C_UDMI(c,t,2) > 0.0000150)
              C_UDMI(c,t,2)=C_UDMI(c,t,2);
       else
              C_UDMI(c,t,2)=0.0000150;

        }
       end_c_loop(c,t)
  }
}

DEFINE_SOURCE(platinum_source,c,t,dS,eqn)                          /*source terms*/
{
return C_UDMI(c,t,3);
}

DEFINE_SOURCE(Na_source,c,t,dS,eqn)
```

```
{
return C_UDMI(c,t,4);
}

/*define the initial carbon loading by setting a value to each cell*/
DEFINE_INIT(CUDMI,d)
{
  Thread *t;
  cell_t c;

  t = Lookup_Thread(d,  BATH_ID);

    begin_c_loop(c,t)
       {
              C_UDMI(c,t,1)=0.00013;                  /*Pt = 3.4 mg for 8 g AC. 25252
CELLS = 3.4/25252 = 0.00013 mg/cell*/
         C_UDMI(c,t,2)=0.00168;                        /*Na = 42 mg for 25252 cells*/
       }
     end_c_loop(c,t)

}
/*end*/
```

Modelling data points

Modelling data points were obtained from fluent output files as shown in the next section

Model U			
Pt Fraction*	Seconds*	Na Fraction	Seconds
0	0	0	0
6.22E-06	300	0.000891	500
1.03E-05	600	0.001529	1000
1.32E-05	900	0.001803	1290
1.58E-05	1200	0.002075	1660
1.92E-05	1500	0.001642	2000
3.04E-05	1750	0.001416	2200
5.15E-05	2000	0.001216	2400
6.82E-05	2200	0.000981	2655
8.27E-05	2400	0.000723	3000
9.70E-05	2665	0.000464	3500
1.06E-04	3000	0.000313	4000
1.07E-04	3155	0.000173	5000
9.79E-05	3680	0.000101	6000
5.74E-05	5180		
3.91E-05	6000		

* See highlighted data points from the modelling data output file (Convergence history of mass fraction of solids (Pt) on outlet)

Model P			
Pt Fraction	Seconds	Na Fraction	Seconds
0	0	0	0
2.31E-05	300	0.001120986	300
3.09E-05	600	0.002044849	600
3.27E-05	900	0.002765186	900
3.27E-05	1200	0.003324588	1200
3.52E-05	1500	0.003758967	1500
7.16E-05	1800	0.002862966	1850
1.51E-04	2250	0.001961626	2300
0.000206	2740	0.001370996	2725
2.10E-04	2890	7.18E-04	3500
2.08E-04	3000	4.73E-04	4000
1.71E-04	3500	2.05E-04	5000
1.21E-04	4000		
7.12E-05	4700		
3.68E-05	5500		
1.05E-05	7000		

Model High			
Pt Fraction	Seconds	Na Fraction	Seconds
0	0	0	0
1.15E-04	300	0.00191426	500
1.53E-04	600	0.003838895	1270
1.60E-04	900	0.004230519	1500
1.57E-04	1200	0.002981775	2000
0.000162	1500	0.002187137	2420
0.000286	1800	0.001569754	2815
0.000563	2190	0.0010597	3260
0.000776	2455	0.000866602	3600
0.001004	2820	0.000656898	4210
0.001075	3140	3.42E-04	5675
0.001071	3260	3.30E-05	10925
0.00105	3600		
0.000918	4120		
4.85E-04	5635		
1.71E-04	8000		
4.70E-05	10925		

Model H			
Pt Fraction	Seconds	Na Fraction	Seconds
0.000000	0	0.000000	0
0.000009	300	0.004487	415
0.000008	600	0.007387	785
0.000008	900	0.006826	890
0.000016	1175	0.005196	1150
0.000030	1355	0.004087	1350
0.000109	1790	0.003201	1550
0.000132	1885	0.002385	1780
0.000157	1985	0.002086	1880
0.000198	2185	0.001809	1985
0.000218	2435	0.001371	2185
0.000188	2785	0.001005	2395
0.000156	2985	0.000747	2585
0.000140	3085	0.000468	2885
0.000125	3195	0.000236	3405
0.000101	3425	0.000126	4100
0.000088	3595	0.000038	5500
0.000081	3695	0.000025	6000
0.000068	3895		
0.000040	4500		
0.000022	5200		
0.000010	6095		
0.000004	7095		

Model AC			
Pt Fraction	Seconds	Na Fraction	Seconds
0.0000000	0	0.0000000	0
0.0000069	300	0.0051842	500
0.0000068	600	0.0080740	870
0.0000060	900	0.0076077	975
0.0000111	1430	0.0055989	1430
0.0000185	1635	0.0035655	1830
0.0000358	1830	0.0021622	2190
0.0001023	2200	0.0015456	2430
0.0001491	2430	0.0009065	2830
0.0001764	2630	0.0005316	3430
0.0001882	2905	0.0002326	4785
0.0001751	3230	0.0001401	5645
0.0001603	3430	0.0000633	7000
0.0000738	4835		
0.0000450	5680		
0.0000208	7000		

Model AD			
Pt Fraction	Seconds	Na Fraction	Seconds
0.0000000	0	0.0000000	0
0.0000082	300	0.0026590	300
0.0000086	600	0.0056666	700
0.0000078	900	0.0085678	1205
0.0000068	1200	0.0045501	2300
0.0000071	1500	0.0015633	3240
0.0000116	1900	0.0006887	3775
0.0000311	2400	0.0005542	3900
0.0001142	3000	0.0002283	4400
0.0001628	3250	0.0000890	5245
0.0001890	3570	0.0000184	7195
0.0001754	3795		
0.0001623	3895		
0.0001145	4195		
0.0000874	4395		
0.0000676	4595		
0.0000539	4795		
0.0000446	4995		
0.0000378	5195		
0.0000075	7195		

Model AB			
Pt Fraction	Seconds	Na Fraction	Seconds
0.000000	0	0.000000	0
0.000010	300	0.003256	500
0.000011	600	0.005748	1000
0.000011	900	0.007016	1330
0.000010	1500	0.006058	1600
0.000014	1800	0.004786	2000
0.000024	2100	0.002644	3000
0.000048	2500	0.001459	4000
0.000096	3000	0.000809	5000
0.000148	3500	0.000148	7885
0.000174	3900		
0.000179	4155		
0.000177	4300		
0.000167	4600		
0.000138	5100		
0.000101	5700		
0.000064	6500		
0.000026	8000		
0.000015	9020		

Model V			
Pt Fraction	Seconds	Na Fraction	Seconds
0.000000	0	0.000000	0
0.000015	300	0.001302	500
0.000022	600	0.002267	1000
0.000025	900	0.002842	1400
0.000026	1200	0.003452	1850
0.000027	1500	0.002680	2355
0.000029	1800	0.002268	2655
0.000035	1955	0.001900	2955
0.000064	2355	0.001679	3155
0.000089	2655	0.001308	3495
0.000114	2955	0.000867	4000
0.000129	3155	0.000778	4200
0.000138	3300	0.000515	5000
0.000146	3580	0.000307	6000
0.000146	4200	0.000183	7000
0.000135	4600	0.000110	8000
0.000118	5000		
0.000095	5500		
0.000075	6000		
0.000058	6500		
0.000041	7200		
0.000027	8000		

Model K			
Pt Fraction	Seconds	Na Fraction	Seconds
0	0	0	0
5.10E-06	300	0.000524	250
1.06E-05	600	0.000972	500
2.54E-05	900	0.001151	620
3.02E-05	1025	0.000895	880
3.64E-05	1300	0.000754	1010
3.76E-05	1520	0.000407	1460
3.85E-05	1815	0.000275	1850
3.85E-05	1850	0.00024	2055
3.82E-05	2100	0.0002	2400
3.67E-05	2400	0.000156	2880
3.30E-05	2800	9.73E-05	3985
2.69E-05	3400	6.75E-05	5000
2.20E-05	4000	4.66E-05	6420
1.78E-05	4600	3.50E-05	7600
1.47E-05	5200	2.14E-05	9640
1.26E-05	5800		7925
1.10E-05	6400		
8.22E-06	7600		
5.06E-06	9600		
4.60E-06	10000		

Model K with higher Na content			
Pt Fraction	Seconds	Na Fraction	Seconds
0.00E+00	0	0.000000	0
3.25E-06	300	0.000484	250
5.47E-06	600	0.000886	500
7.59E-06	900	0.001198	750
1.50E-05	1200	0.001534	1080
2.94E-05	1600	0.001309	1300
3.80E-05	2000	0.000950	1700
4.02E-05	2355	0.000745	2000
4.01E-05	2405	0.000534	2410
3.98E-05	2820	0.000379	3000
3.87E-05	3120	0.000303	3500
3.57E-05	3520	0.000243	4000
3.38E-05	3720	0.000171	5000
3.18E-05	3920	0.000125	6000
2.81E-05	4320	0.000092	7000
2.44E-05	4820	0.000058	8500
2.12E-05	5320	0.000037	10000
1.58E-05	6320		
1.10E-05	7520		
8.15E-06	8500		
5.14E-06	10000		
2.79E-06	12000		
1.51E-06	14000		
8.19E-07	16000		

Example of modelling data output file (Model U – Pt output)

Convergence history of Mass fraction of solids on outlet (in SI units)

Time Step "Area-Weighted Average Mass fraction of solids"

5 1.2223673e-07	305 6.2989343e-06	605 1.0388952e-05	905 1.3277355e-05	1205 1.5811012e-05
10 2.4385443e-07	310 6.3821149e-06	610 1.0444448e-05	910 1.3320167e-05	1210 1.5855223e-05
15 3.6485693e-07	315 6.4646938e-06	615 1.0499621e-05	915 1.3362879e-05	1215 1.5890833e-05
20 4.8524805e-07	320 6.5466761e-06	620 1.0554473e-05	920 1.3405497e-05	1220 1.594441e-05
25 6.0503157e-07	325 6.6280659e-06	625 1.0609009e-05	925 1.3448024e-05	1225 1.5989235e-05
30 7.2421108e-07	330 6.7088681e-06	630 1.0663233e-05	930 1.3490464e-05	1230 1.6034463e-05
35 8.4278997e-07	335 6.7890878e-06	635 1.0717149e-05	935 1.353282e-05	1235 1.6070782e-05
40 9.6077122e-07	340 6.8687291e-06	640 1.0770762e-05	940 1.3575097e-05	1240 1.6125447e-05
45 1.078157e-06	345 6.9477974e-06	645 1.0824074e-05	945 1.3617298e-05	1245 1.6171403e-05
50 1.1949487e-06	350 7.0262972e-06	650 1.0877089e-05	950 1.3659426e-05	1250 1.6217435e-05
55 1.3111467e-06	355 7.1042332e-06	655 1.0929813e-05	955 1.3701487e-05	1255 1.6254551e-05
60 1.4267501e-06	360 7.1816107e-06	660 1.0982249e-05	960 1.3743483e-05	1260 1.6310467e-05
65 1.5417573e-06	365 7.2584348e-06	665 1.10344e-05	965 1.3785419e-05	1265 1.6357264e-05
70 1.6561655e-06	370 7.3347096e-06	670 1.1086271e-05	970 1.3827299e-05	1270 1.639499e-05
75 1.7699709e-06	375 7.41044e-06	675 1.1137866e-05	975 1.3869126e-05	1275 1.6451817e-05
80 1.8831695e-06	380 7.4856316e-06	680 1.1189188e-05	980 1.3910905e-05	1280 1.6499442e-05
85 1.9957563e-06	385 7.5602889e-06	685 1.124024e-05	985 1.3952639e-05	1285 1.6537906e-05
90 2.1077262e-06	390 7.6344168e-06	690 1.1291029e-05	990 1.3994333e-05	1290 1.6595897e-05
95 2.2190736e-06	395 7.7080203e-06	695 1.1341556e-05	995 1.4035991e-05	1295 1.6644493e-05
100 2.3297932e-06	400 7.7811046e-06	700 1.1391827e-05	1000 1.4077616e-05	1300 1.6683776e-05
105 2.4398794e-06	405 7.8536741e-06	705 1.1441844e-05	1005 1.4119213e-05	1305 1.6743024e-05
110 2.5493268e-06	410 7.9257343e-06	710 1.149161e-05	1010 1.4160787e-05	1310 1.6792737e-05
115 2.6581304e-06	415 7.9972888e-06	715 1.1541131e-05	1015 1.420234e-05	1315 1.6832964e-05
120 2.7662848e-06	420 8.068344e-06	720 1.1590411e-05	1020 1.4243878e-05	1320 1.689366e-05
125 2.8737857e-06	425 8.1389035e-06	725 1.1639452e-05	1025 1.4285405e-05	1325 1.6944616e-05
130 2.9806286e-06	430 8.2089728e-06	730 1.1688258e-05	1030 1.4326924e-05	1330 1.6985869e-05
135 3.0868096e-06	435 8.2785573e-06	735 1.1736834e-05	1035 1.4368442e-05	1335 1.7048149e-05
140 3.192325e-06	440 8.3476607e-06	740 1.1785182e-05	1040 1.440996e-05	1340 1.7100467e-05
145 3.2971723e-06	445 8.4162884e-06	745 1.1833308e-05	1045 1.4451485e-05	1345 1.7142844e-05
150 3.4013481e-06	450 8.484446e-06	750 1.1881214e-05	1050 1.4493021e-05	1350 1.7206863e-05
155 3.5048502e-06	455 8.552136e-06	755 1.1928903e-05	1055 1.4534572e-05	1355 1.7260802e-05
160 3.6076767e-06	460 8.6193659e-06	760 1.1976381e-05	1060 1.4576142e-05	1360 1.7304454e-05
165 3.7098262e-06	465 8.6861382e-06	765 1.202365e-05	1065 1.4617737e-05	1365 1.7370465e-05
170 3.8112976e-06	470 8.7524586e-06	770 1.2070714e-05	1070 1.4659361e-05	1370 1.7426013e-05
175 3.9120901e-06	475 8.8183315e-06	775 1.2117577e-05	1075 1.4701019e-05	1375 1.7470944e-05
180 4.0122031e-06	480 8.8837623e-06	780 1.2164242e-05	1080 1.4742715e-05	1380 1.7538929e-05
185 4.1116368e-06	485 8.9487557e-06	785 1.2210714e-05	1085 1.4784455e-05	1385 1.7596181e-05
190 4.2103916e-06	490 9.0133153e-06	790 1.2256995e-05	1090 1.4826242e-05	1390 1.7642637e-05
195 4.3084679e-06	495 9.0774456e-06	795 1.230309e-05	1095 1.4868084e-05	1395 1.771298e-05
200 4.4058665e-06	500 9.141153e-06	800 1.2349002e-05	1100 1.4909983e-05	1400 1.7772265e-05
205 4.502589e-06	505 9.2044402e-06	805 1.2394734e-05	1105 1.4951946e-05	1405 1.7820399e-05
210 4.5986371e-06	510 9.2673126e-06	810 1.2440291e-05	1110 1.4993977e-05	1410 1.7893341e-05
215 4.6940117e-06	515 9.329774e-06	815 1.2485676e-05	1115 1.5036082e-05	1415 1.7954868e-05
220 4.7887161e-06	520 9.3918306e-06	820 1.2530892e-05	1120 1.5078266e-05	1420 1.8004859e-05
225 4.8827515e-06	525 9.4534853e-06	825 1.2575945e-05	1125 1.5120535e-05	1425 1.8080676e-05
230 4.9761206e-06	530 9.5147434e-06	830 1.2620836e-05	1130 1.5162893e-05	1430 1.8144689e-05
235 5.0688263e-06	535 9.5756086e-06	835 1.266557e-05	1135 1.5205347e-05	1435 1.8196741e-05
240 5.1608718e-06	540 9.6360855e-06	840 1.2710149e-05	1140 1.5247902e-05	1440 1.8275756e-05
245 5.2522591e-06	545 9.6961794e-06	845 1.2754579e-05	1145 1.5290565e-05	1445 1.834254e-05
250 5.3429926e-06	550 9.7558941e-06	850 1.2798861e-05	1150 1.533334e-05	1450 1.8396891e-05
255 5.4330749e-06	555 9.8152332e-06	855 1.2843002e-05	1155 1.5376234e-05	1455 1.8479483e-05
260 5.52251e-06	560 9.8742021e-06	860 1.2887003e-05	1160 1.5419253e-05	1460 1.854937e-05
265 5.6113013e-06	565 9.9328054e-06	865 1.2930869e-05	1165 1.5462401e-05	1465 1.8606301e-05
270 5.6994527e-06	570 9.9910458e-06	870 1.2974602e-05	1170 1.550569e-05	1470 1.8692908e-05
275 5.7869679e-06	575 1.0048929e-05	875 1.3018208e-05	1175 1.5548929e-05	1475 1.876629e-05
280 5.873851e-06	580 1.0106458e-05	880 1.3061689e-05	1180 1.5583579e-05	1480 1.8826129e-05
285 5.9601066e-06	585 1.0163639e-05	885 1.3105049e-05	1185 1.5635636e-05	1485 1.8917279e-05
290 6.0457382e-06	590 1.0220474e-05	890 1.3148292e-05	1190 1.5679316e-05	1490 1.899462e-05
295 6.1307505e-06	595 1.0276968e-05	895 1.3191422e-05	1195 1.5722984e-05	1495 1.9057763e-05
300 6.2151476e-06	**600 1.0333126e-05**	**900 1.3234441e-05**	**1200 1.5758143e-05**	**1500 1.9154084e-05**

1505 1.9235946e-05	1825 3.6579873e-05	2145 6.3742082e-05	2465 8.686068e-05	2785 0.00010138367
1510 1.930287e-05	1830 3.6999623e-05	2150 6.4151143e-05	2470 8.7161643e-05	2790 0.00010150883
1515 1.9405128e-05	1835 3.7420337e-05	2155 6.4559244e-05	2475 8.7460256e-05	2795 0.00010169332
1520 1.9492198e-05	1840 3.7841968e-05	2160 6.4966371e-05	2480 8.7756496e-05	2800 0.00010184423
1525 1.9563491e-05	1845 3.8264458e-05	2165 6.5372515e-05	2485 8.8050328e-05	2805 0.00010196423
1530 1.9672634e-05	1850 3.8687755e-05	2170 6.5777647e-05	2490 8.8341738e-05	2810 0.00010214096
1535 1.9765772e-05	1855 3.9111808e-05	2175 6.6181754e-05	2495 8.8630724e-05	2815 0.00010228543
1540 1.9842173e-05	1860 3.9536571e-05	2180 6.658482e-05	2500 8.8917273e-05	2820 0.00010240024
1545 1.9959398e-05	1865 3.9961997e-05	2185 6.6986831e-05	2505 8.9201392e-05	2825 0.00010256921
1550 2.0059693e-05	1870 4.0388029e-05	2190 6.7387766e-05	2510 8.9483074e-05	2830 0.00010270721
1555 2.014215e-05	1875 4.0814633e-05	2195 6.7787616e-05	2515 8.9762332e-05	2835 0.00010281683
1560 2.0269008e-05	1880 4.1241758e-05	**2200 6.8186353e-05**	2520 9.0039168e-05	2840 0.000102978
1565 2.0377891e-05	1885 4.1669358e-05	2205 6.8583489e-05	2525 9.0313602e-05	2845 0.00010310954
1570 2.0467651e-05	1890 4.2097396e-05	2210 6.8979149e-05	2530 9.0585643e-05	2850 0.00010321393
1575 2.0606212e-05	1895 4.2525826e-05	2215 6.9373426e-05	2535 9.0855305e-05	2855 0.00010336731
1580 2.0725613e-05	1900 4.2954613e-05	2220 6.9766349e-05	2540 9.1122602e-05	2860 0.00010349236
1585 2.0824386e-05	1905 4.3383709e-05	2225 7.0157912e-05	2545 9.1385504e-05	2865 0.00010359153
1590 2.0977517e-05	1910 4.3813081e-05	2230 7.0548122e-05	2550 9.1645998e-05	2870 0.0001037371
1595 2.111016e-05	1915 4.4242686e-05	2235 7.0936956e-05	2555 9.1852286e-05	2875 0.00010385566
1600 2.1220387e-05	1920 4.4672495e-05	2240 7.1324386e-05	2560 9.2158021e-05	2880 0.00010394961
1605 2.139227e-05	1925 4.5102464e-05	2245 7.1710383e-05	2565 9.2360686e-05	2885 0.00010408737
1610 2.1541578e-05	1930 4.5532564e-05	2250 7.2094888e-05	2570 9.2661016e-05	2890 0.00010419943
1615 2.1666656e-05	1935 4.5962755e-05	2255 7.2477873e-05	2575 9.2908253e-05	2895 0.00010428815
1620 2.186315e-05	1940 4.6393005e-05	2260 7.2859264e-05	2580 9.3105511e-05	2900 0.0001044181
1625 2.2036227e-05	1945 4.6823283e-05	2265 7.3239025e-05	2585 9.3397852e-05	2905 0.00010452366
1630 2.2182627e-05	1950 4.7253554e-05	2270 7.3617113e-05	2590 9.3638497e-05	2910 0.00010460716
1635 2.2415605e-05	1955 4.7683785e-05	2275 7.3993477e-05	2595 9.383048e-05	2915 0.0001047293
1640 2.2624297e-05	1960 4.811395e-05	2280 7.4368094e-05	2600 9.4115007e-05	2920 0.00010482838
1645 2.2803779e-05	1965 4.8544014e-05	2285 7.4740929e-05	2605 9.4349212e-05	2925 0.00010490666
1650 2.309619e-05	1970 4.8973947e-05	2290 7.5111966e-05	2610 9.4536037e-05	2930 0.00010502099
1655 2.3366934e-05	1975 4.9403723e-05	2295 7.5481177e-05	2615 9.481288e-05	2935 0.00010511359
1660 2.360832e-05	1980 4.983331e-05	2300 7.5848562e-05	2620 9.5040661e-05	2940 0.00010518666
1665 2.4018076e-05	1985 5.0262679e-05	2305 7.6214106e-05	2625 9.5222327e-05	2945 0.0001052932
1670 2.4376117e-05	1990 5.0691808e-05	2310 7.6577802e-05	2630 9.5491465e-05	2950 0.00010537933
1675 2.473691e-05	1995 5.1120667e-05	2315 7.6939657e-05	2635 9.5712661e-05	2955 0.00010544719
1680 2.5100293e-05	**2000 5.1549225e-05**	2320 7.7299665e-05	2640 9.5889241e-05	2960 0.00010554596
1685 2.5466205e-05	2005 5.1977462e-05	2325 7.7657824e-05	2645 9.6150339e-05	2965 0.00010562564
1690 2.5834617e-05	2010 5.240535e-05	2330 7.8014142e-05	2650 9.6365067e-05	2970 0.0001056883
1695 2.6205507e-05	2015 5.2832864e-05	2335 7.8368619e-05	2655 9.6536372e-05	2975 0.00010577933
1700 2.6578853e-05	2020 5.3259973e-05	2340 7.872127e-05	2660 9.678994e-05	2980 0.00010585256
1705 2.6954636e-05	2025 5.3686665e-05	2345 7.9072088e-05	**2665 9.6998352e-05**	2985 0.00010591005
1710 2.7332828e-05	2030 5.4112905e-05	2350 7.934829e-05	2670 9.7164579e-05	2990 0.00010599336
1715 2.77134e-05	2035 5.4538672e-05	2355 7.9758705e-05	2675 9.7410535e-05	2995 0.00010606018
1720 2.8096318e-05	2040 5.4963944e-05	2360 8.0100865e-05	2680 9.7612618e-05	**3000 0.00010611252**
1725 2.8481538e-05	2045 5.5388697e-05	2365 8.0438243e-05	2685 9.7773758e-05	3005 0.00010618813
1730 2.8869013e-05	2050 5.581291e-05	2370 8.0707927e-05	2690 9.8012119e-05	3010 0.00010624857
1735 2.9258696e-05	2055 5.623656e-05	2375 8.110865e-05	2695 9.8207893e-05	3015 0.00010629578
1740 2.9650531e-05	2060 5.6659625e-05	2380 8.143959e-05	2700 9.836426e-05	3020 0.00010636372
1745 3.0044459e-05	2065 5.7082081e-05	2385 8.1705221e-05	2705 9.8595636e-05	3025 0.00010641781
1750 3.0440418e-05	2070 5.7503908e-05	2390 8.2099919e-05	2710 9.8785698e-05	3030 0.00010645992
1755 3.083835e-05	2075 5.7925085e-05	2395 8.2425853e-05	2715 9.8936958e-05	3035 0.00010652024
1760 3.1238189e-05	2080 5.8345591e-05	**2400 8.2687446e-05**	2720 9.9160672e-05	3040 0.000106568
1765 3.1639869e-05	2085 5.8765407e-05	2405 8.3078878e-05	2725 9.9344346e-05	3045 0.00010660503
1770 3.2043321e-05	2090 5.9184509e-05	2410 8.3405626e-05	2730 9.9490477e-05	3050 0.00010665778
1775 3.2448486e-05	2095 5.960288e-05	2415 8.373025e-05	2735 9.97065e-05	3055 0.00010669926
1780 3.2855292e-05	2100 6.0020498e-05	2420 8.4052765e-05	2740 9.9883764e-05	3060 0.0001067313
1785 3.3263677e-05	2105 6.0437349e-05	2425 8.4373183e-05	2745 0.00010002474	3065 0.00010677665
1790 3.3673576e-05	2110 6.0853406e-05	2430 8.4691528e-05	2750 0.00010023302	3070 0.00010681201
1795 3.4084918e-05	2115 6.1268656e-05	2435 8.5007807e-05	2755 0.00010040386	3075 0.00010683902
1800 3.4497647e-05	2120 6.1683073e-05	2440 8.5322012e-05	2760 0.00010053965	3080 0.00010687684
1805 3.4911693e-05	2125 6.2096638e-05	2445 8.5634107e-05	2765 0.00010074018	3085 0.00010690597
1810 3.5327001e-05	2130 6.2509345e-05	2450 8.594407e-05	2770 0.00010090386	3090 0.00010692798
1815 3.5743506e-05	2135 6.2921164e-05	2455 8.625185e-05	2775 0.00010103417	3095 0.00010695834
1820 3.6161149e-05	2140 6.3332081e-05	2460 8.6557397e-05	2780 0.00010122634	3100 0.00010698129

3105 0.00010699834	3425 0.0001044154	3745 9.6013515e-05	4065 8.8863781e-05	4385 8.0687758e-05
3110 0.00010702133	3430 0.00010433893	3750 9.5851618e-05	4070 8.8728251e-05	4390 8.0519319e-05
3115 0.00010703818	3435 0.00010422223	3755 9.5744799e-05	4075 8.8637047e-05	4395 8.0406717e-05
3120 0.00010705034	3440 0.00010414328	3760 9.558595e-05	4080 8.8499721e-05	4400 8.0237507e-05
3125 0.00010706603	3445 0.00010402315	3765 9.5481155e-05	4085 8.8407665e-05	4405 8.0124533e-05
3130 0.0001070768	3450 0.00010394191	3770 9.5326024e-05	4090 8.8268956e-05	4410 7.995456e-05
3135 0.00010708409	3455 0.00010381835	3775 9.5223448e-05	4095 8.8176261e-05	4415 7.9841629e-05
3140 0.00010709249	3460 0.00010373501	3780 9.5071555e-05	4100 8.8036548e-05	4420 7.9671467e-05
3145 0.0001070972	3465 0.00010360838	3785 9.4971343e-05	4105 8.794311e-05	4425 7.9557496e-05
3150 0.00010709965	3470 0.00010352296	3790 9.482295e-05	4110 8.7802357e-05	4430 7.9386242e-05
3155 0.00010710083	3475 0.00010339298	3795 9.4725314e-05	4115 8.770814e-05	4435 7.92723e-05
3160 0.00010709957	3480 0.00010330531	3800 9.4579002e-05	4120 8.7566244e-05	4440 7.9101708e-05
3165 0.00010709724	3485 0.00010317191	3805 9.4482588e-05	4125 8.7471271e-05	4445 7.8987759e-05
3170 0.0001070913	3490 0.00010308187	3810 9.4339863e-05	4130 8.7328226e-05	4450 7.8816069e-05
3175 0.00010708415	3495 0.00010294525	3815 9.424561e-05	4135 8.7232482e-05	4455 7.8701712e-05
3180 0.00010707709	3500 0.00010285339	3820 9.410653e-05	4140 8.7088309e-05	4460 7.8529862e-05
3185 0.0001070641	3505 0.00010271375	3825 9.4014729e-05	4145 8.6991764e-05	4465 7.8415105e-05
3190 0.00010705111	3510 0.00010261952	3830 9.3878305e-05	4150 8.6846238e-05	4470 7.824268e-05
3195 0.00010703937	3515 0.0001024768	3835 9.378817e-05	4155 8.6748987e-05	4475 7.8127552e-05
3200 0.0001070229	3520 0.00010238039	3840 9.3654111e-05	4160 8.6602442e-05	4480 7.7954581e-05
3205 0.00010700065	3525 0.00010223433	3845 9.3565446e-05	4165 8.6504355e-05	4485 7.7839104e-05
3210 0.00010697998	3530 0.00010213583	3850 9.3433438e-05	4170 8.635666e-05	4490 7.7665631e-05
3215 0.00010695741	3535 0.00010201117	3855 9.3346047e-05	4175 8.6258013e-05	4495 7.7549819e-05
3220 0.00010693801	3540 0.00010186063	3860 9.3215793e-05	4180 8.6109198e-05	4500 7.7375866e-05
3225 0.00010691204	3545 0.00010175888	3865 9.3129471e-05	4185 8.6009582e-05	4505 7.7259749e-05
3230 0.0001068842	3550 0.00010160516	3870 9.3000686e-05	4190 8.5859603e-05	4510 7.7085337e-05
3235 0.00010685448	3555 0.00010150143	3875 9.2915259e-05	4195 8.5759246e-05	4515 7.6968921e-05
3240 0.00010681638	3560 0.00010134489	3880 9.2787668e-05	4200 8.5608139e-05	4520 7.679408e-05
3245 0.00010678259	3565 0.00010123936	3885 9.270294e-05	4205 8.5507032e-05	4525 7.6677388e-05
3250 0.00010674705	3570 0.00010107974	3890 9.2576294e-05	4210 8.5354819e-05	4530 7.650214e-05
3255 0.00010670978	3575 0.00010097228	3895 9.2492111e-05	4215 8.5252854e-05	4535 7.6385186e-05
3260 0.00010667069	3580 0.00010080852	3900 9.2366157e-05	4220 8.509952e-05	4540 7.6209551e-05
3265 0.00010662979	3585 0.00010069877	3905 9.2282367e-05	4225 8.4996944e-05	4545 7.6092343e-05
3270 0.00010658698	3590 0.00010053244	3910 9.2156901e-05	4230 8.484257e-05	4550 7.5916352e-05
3275 0.00010654248	3595 0.00010042021	3915 9.2073358e-05	4235 8.4739273e-05	4555 7.5798918e-05
3280 0.00010650545	3600 0.00010025072	3920 9.1948168e-05	4240 8.4583808e-05	4560 7.5622585e-05
3285 0.00010645763	3605 0.00010013675	3925 9.1864757e-05	4245 8.4479812e-05	4565 7.5504933e-05
3290 0.00010639786	3610 9.9965298e-05	3930 9.1739726e-05	4250 8.4323314e-05	4570 7.5328287e-05
3295 0.00010634605	3615 9.9850382e-05	3935 9.1656322e-05	4255 8.4218642e-05	4575 7.5210432e-05
3300 0.00010629251	3620 9.9676392e-05	3940 9.1531227e-05	4260 8.4061146e-05	4580 7.5033495e-05
3305 0.00010624861	3625 9.9560202e-05	3945 9.1447728e-05	4265 8.3955907e-05	4585 7.491545e-05
3310 0.00010618049	3630 9.9384255e-05	3950 9.1322399e-05	4270 8.3797422e-05	4590 7.4738236e-05
3315 0.00010613387	3635 9.9265781e-05	3955 9.123877e-05	4275 8.3691899e-05	4595 7.4620009e-05
3320 0.00010606194	3640 9.9087069e-05	3960 9.1113157e-05	4280 8.3532432e-05	4600 7.4442542e-05
3325 0.00010601269	3645 9.8967132e-05	3965 9.1029251e-05	4285 8.3425795e-05	4605 7.4324162e-05
3330 0.00010593676	3650 9.8785444e-05	3970 9.0903181e-05	4290 8.3265382e-05	4610 7.4146461e-05
3335 0.00010588478	3655 9.8663477e-05	3975 9.0818918e-05	4295 8.3158113e-05	4615 7.4027921e-05
3340 0.0001058048	3660 9.8479461e-05	3980 9.0692221e-05	4300 8.2996783e-05	4620 7.3850002e-05
3345 0.00010573598	3665 9.8355384e-05	3985 9.0607573e-05	4305 8.2888932e-05	4625 7.3731331e-05
3350 0.00010567977	3670 9.8168864e-05	3990 9.0480273e-05	4310 8.2726649e-05	4630 7.3553208e-05
3355 0.00010560786	3675 9.8043645e-05	3995 9.03951e-05	4315 8.2618171e-05	4635 7.3434407e-05
3360 0.0001055344	**3680 9.7854259e-05**	4000 9.0266949e-05	4320 8.2455022e-05	4640 7.3256102e-05
3365 0.00010545919	3685 9.7700758e-05	4005 9.0181231e-05	4325 8.2345978e-05	4645 7.3137191e-05
3370 0.00010538236	3690 9.7550444e-05	4010 9.0052221e-05	4330 8.2181992e-05	4650 7.2958726e-05
3375 0.00010528795	3695 9.7401928e-05	4015 8.9965914e-05	4335 8.2072402e-05	4655 7.2839706e-05
3380 0.00010522422	3700 9.7254648e-05	4020 8.9835979e-05	4340 8.1909151e-05	4660 7.2661096e-05
3385 0.00010512644	3705 9.7108285e-05	4025 8.9749039e-05	4345 8.1799597e-05	4665 7.2541981e-05
3390 0.0001050598	3710 9.6962627e-05	4030 8.9618137e-05	4350 8.1634156e-05	4670 7.236324e-05
3395 0.00010495803	3715 9.6817566e-05	4035 8.9530535e-05	4355 8.1523598e-05	4675 7.2244053e-05
3400 0.0001048889	3720 9.6675991e-05	4040 8.9398607e-05	4360 8.1357364e-05	4680 7.2065195e-05
3405 0.00010478335	3725 9.6564007e-05	4045 8.9310313e-05	4365 8.1246282e-05	4685 7.1945935e-05
3410 0.00010471168	3730 9.6397111e-05	4050 8.9177374e-05	4370 8.1079292e-05	4690 7.1766983e-05
3415 0.0001046024	3735 9.6286618e-05	4055 8.9088411e-05	4375 8.0967635e-05	4695 7.1647657e-05
3420 0.00010452834	3740 9.6122232e-05	4060 8.8954344e-05	4380 8.0799902e-05	4700 7.1468625e-05
4705 7.1349255e-05	5025 6.1849845e-05	5345 5.3067273e-05	5665 4.5828947e-05	5985 3.9440376e-05

4710 7.1170158e-05
4715 7.1050745e-05
4720 7.0871603e-05
4725 7.0752161e-05
4730 7.0572976e-05
4735 7.0453527e-05
4740 7.0274335e-05
4745 7.0154871e-05
4750 6.9975671e-05
4755 6.9856214e-05
4760 6.9677029e-05
4765 6.9557587e-05
4770 6.9378424e-05
4775 6.9259004e-05
4780 6.9079884e-05
4785 6.89605e-05
4790 6.8781439e-05
4795 6.8662092e-05
4800 6.8483103e-05
4805 6.8363814e-05
4810 6.8184905e-05
4815 6.8065674e-05
4820 6.788686e-05
4825 6.7767702e-05
4830 6.7589004e-05
4835 6.7469926e-05
4840 6.7291359e-05
4845 6.7172361e-05
4850 6.6993918e-05
4855 6.6875022e-05
4860 6.6696739e-05
4865 6.6577944e-05
4870 6.6399822e-05
4875 6.6281136e-05
4880 6.6103188e-05
4885 6.5984619e-05
4890 6.5806213e-05
4895 6.5686487e-05
4900 6.5507251e-05
4905 6.5387983e-05
4910 6.5209271e-05
4915 6.5090215e-05
4920 6.4911772e-05
4925 6.4792905e-05
4930 6.4614738e-05
4935 6.449606e-05
4940 6.4318498e-05
4945 6.4199856e-05
4950 6.4021784e-05
4955 6.3903179e-05
4960 6.372542e-05
4965 6.3607025e-05
4970 6.3429579e-05
4975 6.3311389e-05
4980 6.3134255e-05
4985 6.3016283e-05
4990 6.283947e-05
4995 6.2721709e-05
5000 6.2546482e-05
5005 6.2430197e-05
5010 6.2255895e-05
5015 6.2139792e-05
5020 6.1965766e-05
5030 6.167611e-05
5035 6.1560393e-05
5040 6.1386956e-05
5045 6.1271443e-05
5050 6.1098319e-05
5055 6.0983017e-05
5060 6.081022e-05
5065 6.0695143e-05
5070 6.052143e-05
5075 6.0405335e-05
5080 6.0231388e-05
5085 6.0115563e-05
5090 5.9942027e-05
5095 5.9826489e-05
5100 5.9653379e-05
5105 5.9538121e-05
5110 5.9365437e-05
5115 5.9250466e-05
5120 5.9078218e-05
5125 5.8963535e-05
5130 5.8791717e-05
5135 5.8677328e-05
5140 5.8506117e-05
5145 5.8392019e-05
5150 5.8221412e-05
5155 5.8107933e-05
5160 5.793793e-05
5165 5.7824753e-05
5170 5.7655205e-05
5175 5.7542329e-05
5180 5.7373243e-05
5185 5.7260939e-05
5190 5.7093828e-05
5195 5.6982826e-05
5200 5.6816847e-05
5205 5.6706529e-05
5210 5.6541536e-05
5215 5.6432284e-05
5220 5.626951e-05
5225 5.6161312e-05
5230 5.5999506e-05
5235 5.5891971e-05
5240 5.5731194e-05
5245 5.5624369e-05
5250 5.5464698e-05
5255 5.535864e-05
5260 5.5200151e-05
5265 5.5094901e-05
5270 5.4937653e-05
5275 5.4833243e-05
5280 5.4677996e-05
5285 5.4574924e-05
5290 5.4420991e-05
5295 5.4318771e-05
5300 5.4166074e-05
5305 5.4064629e-05
5310 5.3913045e-05
5315 5.381239e-05
5320 5.3661992e-05
5325 5.3562118e-05
5330 5.3412874e-05
5335 5.3313768e-05
5340 5.3165651e-05
5350 5.2920237e-05
5355 5.2822565e-05
5360 5.2676565e-05
5365 5.2579566e-05
5370 5.243456e-05
5375 5.2338208e-05
5380 5.219414e-05
5385 5.2098399e-05
5390 5.1955212e-05
5395 5.1860061e-05
5400 5.1717681e-05
5405 5.1623014e-05
5410 5.1481442e-05
5415 5.1387353e-05
5420 5.1246629e-05
5425 5.1153111e-05
5430 5.1013161e-05
5435 5.0920153e-05
5440 5.0780945e-05
5445 5.0688417e-05
5450 5.0549952e-05
5455 5.0457875e-05
5460 5.0320075e-05
5465 5.0228442e-05
5470 5.0091221e-05
5475 5.0000006e-05
5480 4.9863367e-05
5485 4.9772483e-05
5490 4.9636434e-05
5495 4.9545939e-05
5500 4.9410464e-05
5505 4.9320348e-05
5510 4.9185437e-05
5515 4.9095735e-05
5520 4.8961421e-05
5525 4.8872171e-05
5530 4.8738602e-05
5535 4.8649643e-05
5540 4.8516355e-05
5545 4.8427752e-05
5550 4.8294718e-05
5555 4.8206184e-05
5560 4.8073842e-05
5565 4.7985828e-05
5570 4.7853664e-05
5575 4.7765803e-05
5580 4.7634505e-05
5585 4.7547266e-05
5590 4.7416488e-05
5595 4.7329431e-05
5600 4.7199326e-05
5605 4.7112779e-05
5610 4.6983016e-05
5615 4.6896799e-05
5620 4.6767698e-05
5625 4.6681802e-05
5630 4.6553181e-05
5635 4.6467438e-05
5640 4.6339213e-05
5645 4.6253877e-05
5650 4.6126206e-05
5655 4.6041263e-05
5660 4.5913654e-05
5670 4.5701792e-05
5675 4.5617122e-05
5680 4.5490757e-05
5685 4.540661e-05
5690 4.5280591e-05
5695 4.519675e-05
5700 4.5071214e-05
5705 4.4987682e-05
5710 4.4862601e-05
5715 4.4779372e-05
5720 4.4655073e-05
5725 4.4572123e-05
5730 4.4447912e-05
5735 4.4365301e-05
5740 4.4241562e-05
5745 4.4159216e-05
5750 4.4035976e-05
5755 4.3953925e-05
5760 4.38311e-05
5765 4.3749369e-05
5770 4.3627009e-05
5775 4.3545599e-05
5780 4.3423657e-05
5785 4.3342534e-05
5790 4.3221236e-05
5795 4.3140419e-05
5800 4.3019714e-05
5805 4.2939162e-05
5810 4.2818549e-05
5815 4.2738171e-05
5820 4.2617983e-05
5825 4.2538144e-05
5830 4.2418782e-05
5835 4.2339379e-05
5840 4.2220425e-05
5845 4.2141248e-05
5850 4.2022639e-05
5855 4.1943698e-05
5860 4.1825493e-05
5865 4.1746753e-05
5870 4.1629046e-05
5875 4.1550597e-05
5880 4.1433144e-05
5885 4.1355113e-05
5890 4.123828e-05
5895 4.1160547e-05
5900 4.104415e-05
5905 4.0966705e-05
5910 4.0850766e-05
5915 4.0773641e-05
5920 4.0658109e-05
5925 4.0581232e-05
5930 4.046613e-05
5935 4.038955e-05
5940 4.0274906e-05
5945 4.0198527e-05
5950 4.0084025e-05
5955 4.0007933e-05
5960 3.9893865e-05
5965 3.9817976e-05
5970 3.9704555e-05
5975 3.9628965e-05
5980 3.9515675e-05
5990 3.9327526e-05
5995 3.9252278e-05
6000 3.9139948e-05
6005 3.9065111e-05
6010 3.8953291e-05
6015 3.8878872e-05
6020 3.8767572e-05
6025 3.8693659e-05
6030 3.8582606e-05
6035 3.8508675e-05
6040 3.8398197e-05
6045 3.8324761e-05
6050 3.8214839e-05
6055 3.814181e-05
6060 3.8032369e-05
6065 3.7959431e-05
6070 3.7850252e-05
6075 3.7777594e-05
6080 3.7668789e-05
6085 3.7596415e-05
6090 3.7488062e-05
6095 3.7416023e-05
6100 3.730812e-05
6105 3.723631e-05
6110 3.7128881e-05
6115 3.7057311e-05
6120 3.695031e-05
6125 3.6879053e-05
6130 3.6772351e-05
6135 3.6701364e-05
6140 3.6595182e-05
6145 3.6524489e-05
6150 3.6418634e-05
6155 3.6348305e-05
6160 3.6242902e-05
6165 3.6172776e-05
6170 3.6067799e-05
6175 3.599796e-05
6180 3.5893416e-05

Appendix D

Calculations and fitting of models

Modelling Isotherms

Freundlich Isotherm

The Freundlich isotherm models were fitted to the equilibrium data, by linearizing Eq.4.1 by taking the log of the values as per Eq. D1

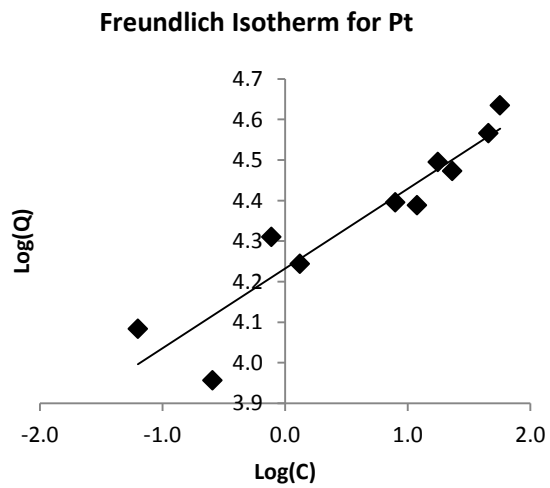
$$Q = AC^n \quad (4.1)$$

$$Log(Q) = Log(A) + nLog(C) \quad (D1)$$

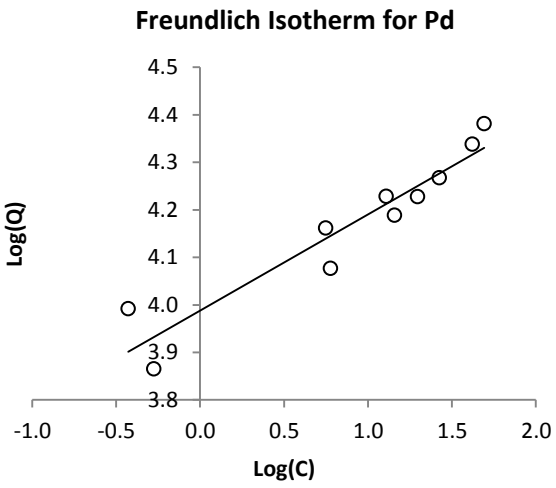
Log Q was plotted against Log C and linear trend lines were then fitted to the data to obtain the constants of the model.

	Pt (mg/L)	Loading (mg/kg)	Freundlich Isotherm for Pt Log Qe	Log Ce
Pt 0.6g/L AC 30ppm	17.6	31283.3	4.5	1.2
Pt 1g/L AC 30ppm	12.0	24450.0	4.4	1.1
2g/L AC 30ppm	1.3	17541.5	4.2	0.1
Pt 3g/L AC 30ppm	0.1	12115.6	4.1	-1.2
Pt 4g/L AC 30ppm	0.3	9038.5	4.0	-0.6
Pt 0.6g/L 70ppm	56.7	43116.7	4.6	1.8
Pt 1g/L AC 70ppm	45.7	36810.0	4.6	1.7
Pt 2g/L AC 70ppm	23.1	29710.0	4.5	1.4
Pt 3g/L AC 70ppm	7.9	24868.0	4.4	0.9
Pt 4g/L AC 70ppm	0.8	20439.0	4.3	-0.1

	Pd (mg/L)	Loading (mg/kg)	Freundlich Isotherm for Pd Log Qe	Log Ce
Pd 0.6g/L 30ppm	19.7	16900.0	4.2	1.3
Pd 1g/L 30ppm	14.4	15440.0	4.2	1.2
Pd 2g/L 30ppm	6.0	11936.0	4.1	0.8
Pd 3g/L 30ppm	0.4	9822.4	4.0	-0.4
Pd 4g/L 30ppm	0.5	7327.5	3.9	-0.3
Pd 0.6g/L 64ppm	49.2	24050.0	4.4	1.7
Pd 1g/L 64ppm	41.8	21800.0	4.3	1.6
Pd 2g/L 64ppm	26.6	18505.0	4.3	1.4
Pd 3g/L 64ppm	12.8	16933.3	4.2	1.1
Pd 4g/L 64ppm	5.6	14505.8	4.2	0.7



y = 0.1969x + 4.2322
R² = 0.8744



y = 0.2026x + 3.9881
R² = 0.8969

Langmuir isotherms

The Langmuir isotherm models were fitted to the equilibrium data, by linearizing Eq.4.2 as per Eq. D2

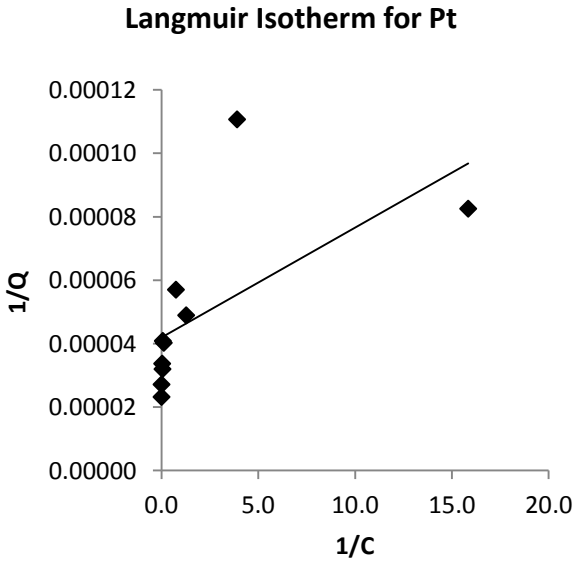
$$Q = \frac{Q_m KC}{1+KC} \tag{4.2}$$

$$\frac{1}{Q} = \left(\frac{1}{KQ_m}\right)\frac{1}{C} + \frac{1}{C} \tag{D1}$$

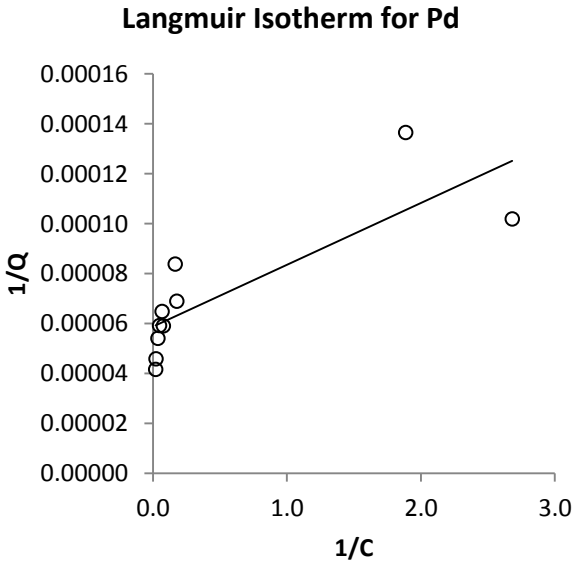
By plotting 1/Q against 1/C for the Langmuir isotherm, linear trend lines did not show a fit for the data.

			Langmuir isotherm for Pt	
	Pt (mg/L)	Loading (mg/kg)	1/Q	1/C
Pt 0.6g/L AC 30ppm	17.6	31283.3	0.00003	0.1
Pt 1g/L AC 30ppm	12.0	24450.0	0.00004	0.1
2g/L AC 30ppm	1.3	17541.5	0.00006	0.8
Pt 3g/L AC 30ppm	0.1	12115.6	0.00008	15.8
Pt 4g/L AC 30ppm	0.3	9038.5	0.00011	3.9
Pt 0.6g/L 70ppm	56.7	43116.7	0.00002	0.0
Pt 1g/L AC 70ppm	45.7	36810.0	0.00003	0.0
Pt 2g/L AC 70ppm	23.1	29710.0	0.00003	0.0
Pt 3g/L AC 70ppm	7.9	24868.0	0.00004	0.1
Pt 4g/L AC 70ppm	0.8	20439.0	0.00005	1.3

			Langmuir isotherm for Pd	
	Pd (mg/L)	Loading (mg/kg)	1/Q	1/C
Pd 0.6g/L 30ppm	19.7	16900.0	0.00006	0.1
Pd 1g/L 30ppm	14.4	15440.0	0.00006	0.1
Pd 2g/L 30ppm	6.0	11936.0	0.00008	0.2
Pd 3g/L 30ppm	0.4	9822.4	0.00010	2.7
Pd 4g/L 30ppm	0.5	7327.5	0.00014	1.9
Pd 0.6g/L 64ppm	49.2	24050.0	0.00004	0.0
Pd 1g/L 64ppm	41.8	21800.0	0.00005	0.0
Pd 2g/L 64ppm	26.6	18505.0	0.00005	0.0
Pd 3g/L 64ppm	12.8	16933.3	0.00006	0.1
Pd 4g/L 64ppm	5.6	14505.8	0.00007	0.2



y = 3E-06x + 4E-05
R² = 0.3872



y = 2E-05x + 6E-05
R² = 0.6638

Kinetic adsorption models

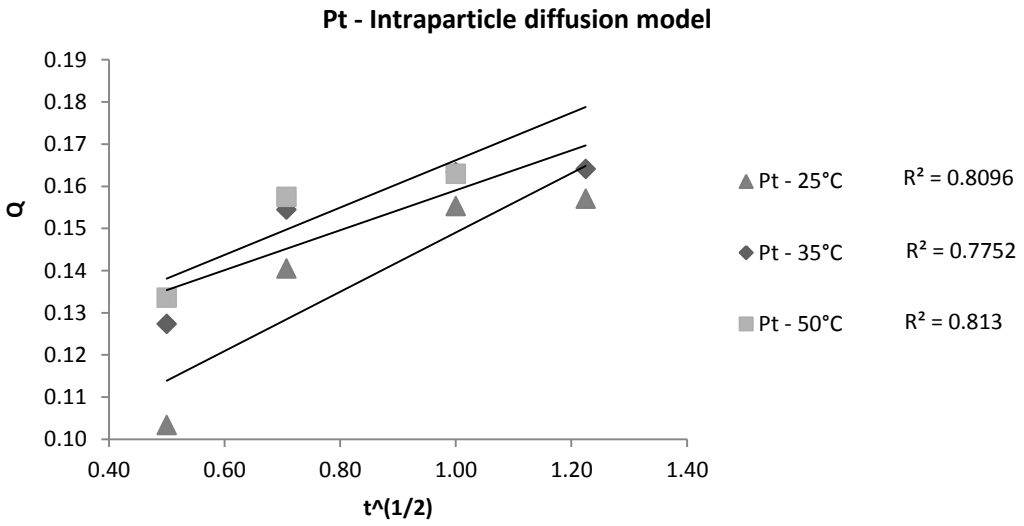
Intra-particle diffusion plot (Vimonses et al. 2009)

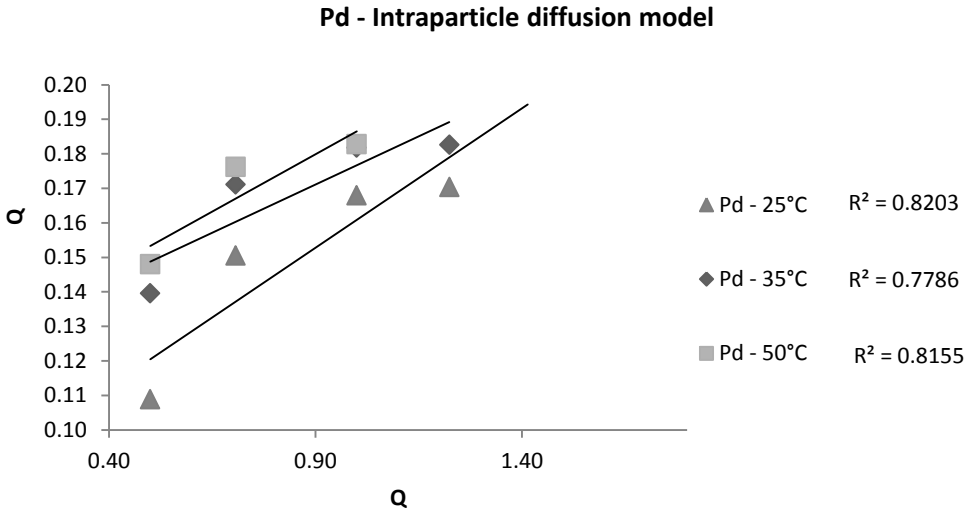
$$q_t = k_{id} t^{1/2} + C_{id}$$

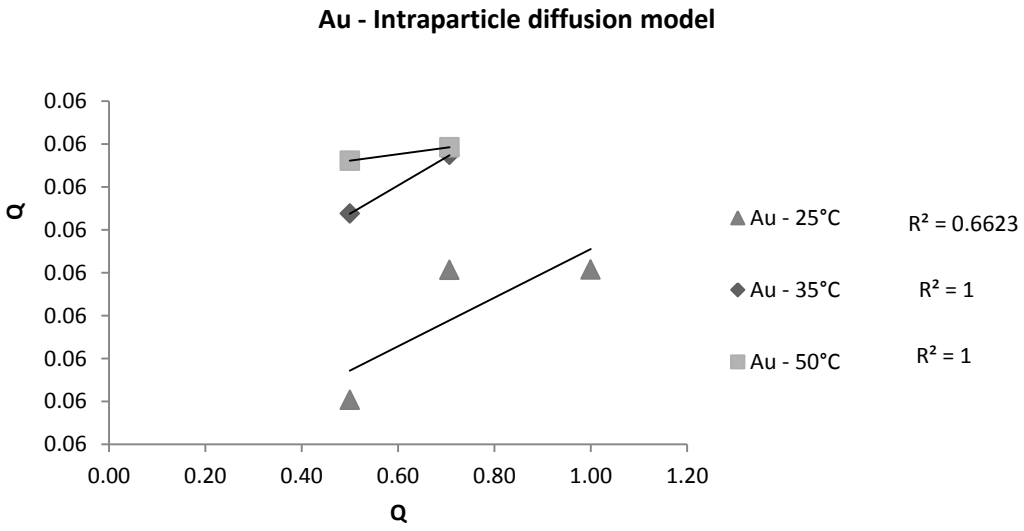
	Time (hrs)	Analysis - ICP MS (mg/L) Na	Pt	Pd	Au	Pt qt	Pd qt	Au qt	t^(1/2)
LT 25:1	0.0	399.0	0.79	0.85	0.30				
LT 25:2	0.3	413.0	0.27	0.31	0.01	0.10	0.11	0.06	0.50
LT 25:3	0.5	405.6	0.08	0.10	0.00	0.14	0.15	0.06	0.71
LT 25:4	1.0	397.1	0.01	0.01	0.00	0.16	0.17	0.06	1.00
LT 25:5	1.5	399.4	0.00	0.00	0.00	0.16	0.17		1.22
LT 25:6	2.0	396.5	0.00	0.00	0.00				1.41
LT 25:7	3.0	401.2	0.00	0.00	0.00				

	Time (hrs)	Analysis - ICP MS (mg/L) Na	Pt	Pd	Au	Pt qt	Pd qt	Au qt	t^(1/2)
LT 35:1	0	406.6	0.82	0.91	0.31				
LT 35:2	0.25	396.4	0.18	0.22	0.00	0.13	0.14	0.06	0.50
LT 35:3	0.5	397.9	0.05	0.06	0.00	0.15	0.17	0.06	0.71
LT 35:4	1	404.2	0.00	0.01	0.01	0.16	0.18		1.00
LT 35:5	1.5	409.2	0.00	0.00	0.00	0.16	0.18		1.22
LT 35:6	2	408.8	0.00	0.00	0.00				
LT 35:7	3	401.1	0.00	0.00	0.00				

	Time (hrs)	Analysis - ICP MS (mg/L) Na	Pt	Pd	Au	Pt qt	Pd qt	Au qt	t^(1/2)
LT 50:1	0	407.9	0.82	0.92	0.31				
LT 50:2	0.25	413.1	0.15	0.18	0.00	0.13	0.15	0.06	0.50
LT 50:3	0.5	413.3	0.03	0.04	0.00	0.16	0.18	0.06	0.71
LT 50:4	1	420.2	0.00	0.01	0.00	0.16	0.18		1.00
LT 50:5	1.5	420.3	0.00	0.00	0.00		0.18		1.22
LT 50:6	2	407.2	0.00	0.00	0.00				
LT 50:7	3	410.3	0.00	0.00	0.00				







Second order model (Ho, 2006)

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

k = the rate constant of adsorption (g/mg hr),

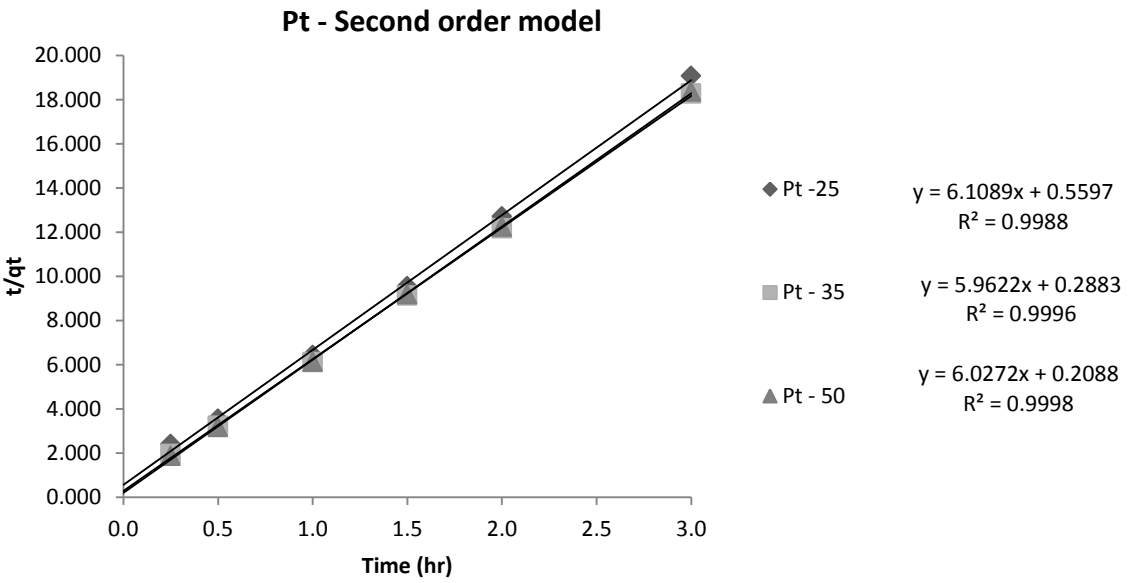
qe = amount of divalent metal ions adsorbed at equilibrium (mg/g),

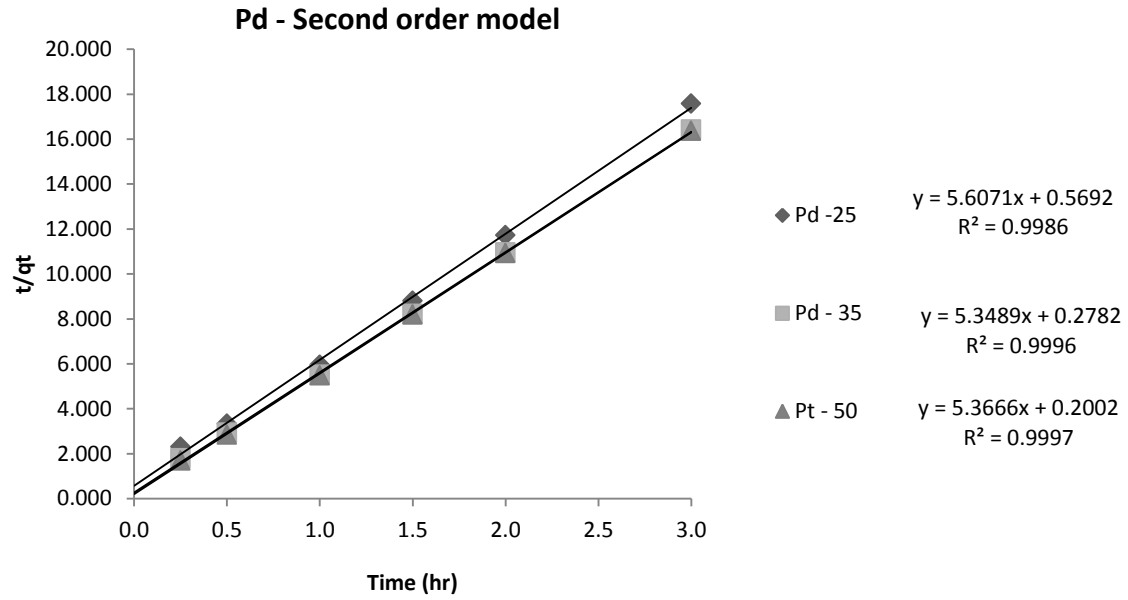
The model constants can be determined experimentally by plotting t/qt against t.

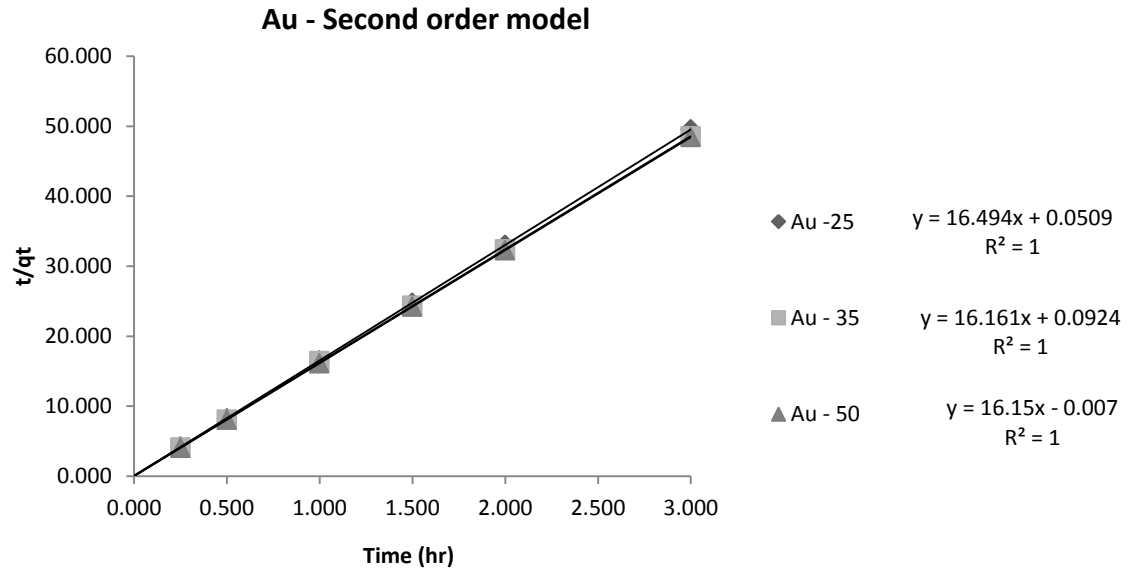
		Analysis - ICP MS (mg/L)				Pt		Pd		Au	
	Time (hrs)	Na	Pd	Pt	Au	q_t	t/q_t	q_t	t/q_t	q_t	t/q_t
LT 25:1	0.000	399.000	0.854	0.787	0.303						
LT 25:2	0.250	413.000	0.309	0.270	0.008	0.103	2.418	0.109	2.296	0.059	4.236
LT 25:3	0.500	405.600	0.101	0.084	0.000	0.140	3.559	0.150	3.323	0.061	8.260
LT 25:4	1.000	397.100	0.014	0.010	0.000	0.155	6.440	0.168	5.954	0.061	16.519
LT 25:5	1.500	399.400	0.002	0.001	0.000	0.157	9.551	0.170	8.805	0.061	24.778
LT 25:6	2.000	396.500	0.000	0.000	0.000	0.157	12.717	0.171	11.720	0.061	33.033
LT 25:7	3.000	401.200	0.000	0.000	0.000	0.157	19.070	0.171	17.575	0.061	49.551

		Analysis - ICP MS (mg/L)				Pt		Pd		Au	
	Time (hrs)	Na	Pd	Pt	Au	q_t	t/q_t	q_t	t/q_t	q_t	t/q_t
LT 35:1	0.000	406.600	0.914	0.821	0.309						
LT 35:2	0.250	396.400	0.216	0.184	0.003	0.127	1.962	0.140	1.791	0.061	4.086
LT 35:3	0.500	397.900	0.059	0.049	0.000	0.154	3.237	0.171	2.923	0.062	8.081
LT 35:4	1.000	404.200	0.005	0.004	0.005	0.163	6.121	0.182	5.502	0.061	16.441
LT 35:5	1.500	409.200	0.001	0.001	0.001	0.164	9.141	0.183	8.215	0.062	24.343
LT 35:6	2.000	408.800	0.000	0.000	0.001	0.164	12.183	0.183	10.947	0.062	32.387
LT 35:7	3.000	401.100	0.000	0.000	0.000	0.164	18.273	0.183	16.420	0.062	48.548

		Analysis - ICP MS (mg/L)				Pt		Pd		Au	
	Time (hrs)	Na	Pd	Pt	Au	q_t	t/q_t	q_t	t/q_t	q_t	t/q_t
LT 50:1	0.000	407.90	0.919	0.819	0.310						
LT 50:2	0.250	413.10	0.180	0.151	0.001	0.134	1.872	0.148	1.690	0.062	4.045
LT 50:3	0.500	413.30	0.038	0.031	0.000	0.158	3.174	0.176	2.838	0.062	8.069
LT 50:4	1.000	420.20	0.006	0.004	0.000	0.163	6.136	0.183	5.472	0.062	16.138
LT 50:5	1.500	420.30	0.004	0.003	0.000	0.163	9.188	0.183	8.193	0.062	24.207
LT 50:6	2.000	407.20	0.003	0.002	0.000	0.163	12.246	0.183	10.917	0.062	32.273
LT 50:7	3.000	410.30	0.003	0.002	0.000	0.163	18.361	0.183	16.367	0.062	48.460







Pt

T (°C)	Slope	q_e (mg/g)	q_e (mg/kg)	1/h	h (mg/g h)	k (g/mg h)	ln(k)	1000/T
25	6.109	0.164	164	0.560	1.787	66.676	4.200	3.356
35	5.962	0.168	168	0.288	3.469	123.302	4.815	3.247
50	6.027	0.166	166	0.209	4.789	173.981	5.159	3.096

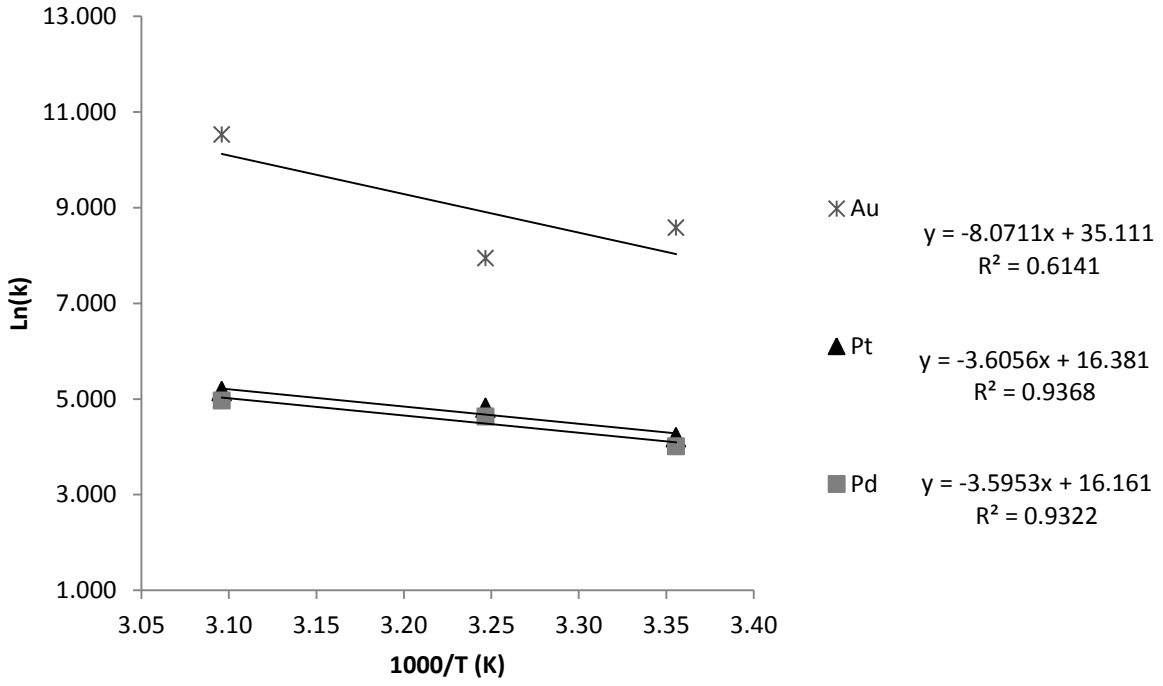
Pd

T (°C)	Slope	q_e (mg/g)	q_e (mg/kg)	1/h	h (mg/g h)	k (g/mg h)	ln(k)	1000/T
25	5.607	0.178	178	0.569	1.757	55.235	4.012	3.356
35	5.349	0.187	187	0.278	3.595	102.842	4.633	3.247
50	5.367	0.186	186	0.200	4.995	143.858	4.969	3.096

Au

T (°C)	Slope	q_e (mg/g)	q_e (mg/kg)	1/h	h (mg/g h)	k (g/mg h)	ln(k)	1000/T
25	16.494	0.061	61	0.051	19.646	5344.834	8.584	3.356
35	16.161	0.062	62	0.092	10.823	2826.601	7.947	3.247
50	16.150	0.062	62	0.007	142.857	37260.357	10.526	3.096

Arhenius Plot from second order model



Activation energy calculated by Second order model

	E_{act}	
	kJ/mol	kcal/mol
Pd	29.9	7.1
Pt	30.0	7.2
Au	67.1	16.0

Recovery calculation

The calculation of the recoveries for the elution experiments were done by calculating the area underneath the elution concentration curve by means of the trapezoidal rule which is an approximate technique for calculating the definite integral and works by approximating the region under the graph of the function f(x) as a trapezoid and calculating its area according to:

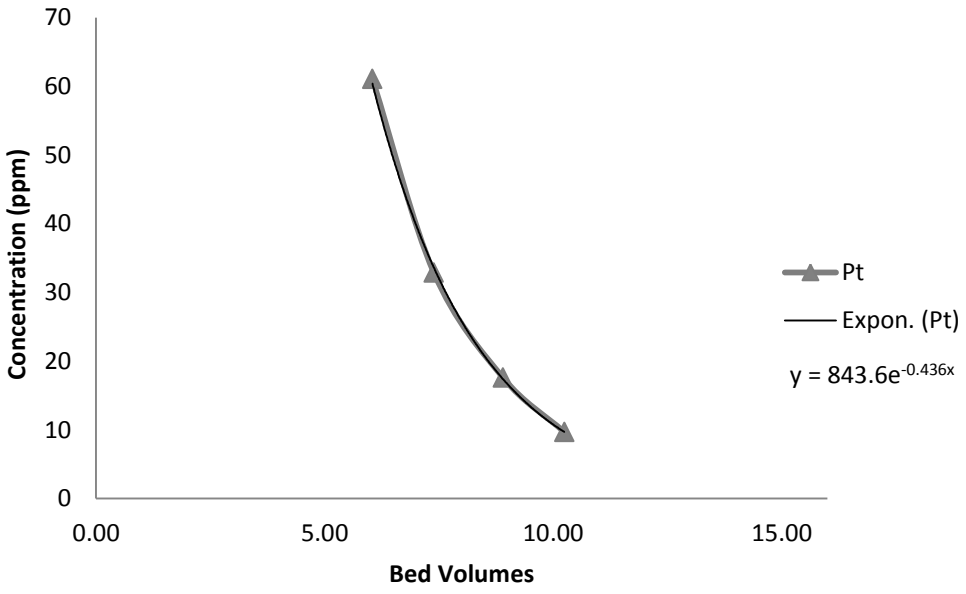
$$\int_a^b f(x)dx \approx (b-a)\frac{f(b)+f(a)}{2}$$

The 100% recovery mark was calculated by adding a trend line to the last points of the elution curve and predicting the amount of bed volumes where 100% elution of the PGMs occurs. In the case of an exponential curve as in the example below, the bed volumes were calculated by assuming a PGM concentration value close to zero (0.01mg/L).

$y = 843.6e^{-0.405x}$

$0.01 = 843.6e^{-0.405x}$

$x = 28$



It is assumed here that all the PGMs are eluted from the activated carbon. The amount of PGMs calculated by the above mentioned method exceed the amount of PGMs that are calculated from the amount loaded onto activated the carbon which gives some confidence to the assumption that PGMs are eluted from the activated carbon to completion.

Appendix E

Publications and conferences

Refereed Articles

Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J,. 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. South African Journal of Mining and Minerals. Vol 113. May 2013. pp 381 – 388

Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J, 2014. The effect of temperature, cyanide and base metals on the adsorption of Pt, Pd and Au onto activated carbon, Hydrometallurgy, Vol 149, pp 132–142

Peer Reviewed Conference Proceedings

Snyders, C.A, Mpinga, N, Bradshaw, S.M, Akdogan, G, Eksteen J.J, The adsorption and elution of platinum group metals from cyanide leach solutions using activated carbon, *The Southern African Institute of Mining and Metallurgy Platinum 2012*, Sun City, South Africa, 18 - 22 Sept 2012, pp 743 Volume II

Cornelius A Snyders, Steven M Bradshaw, Guven Akdogan, Cleophace N Mpinga, Andries P Van Wyk, Jacques J Eksteen, 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. IMPC, Santiago, Chile, 20 -24 October 2014.

Eksteen, J.J., Mwase, J.M., Peterson, J., Bradshaw, S.M., Akdogan, G., Mpinga, N., **Snyders, C.A**. 2014. A novel, energy efficient, two stage heap leach process for the extraction and recovery of PGMs**.** IMPC, Santiago, Chile, 20 -24 October 2014.

Conference Proceedings

Eksteen, J.J., Mwase, J.M., Peterson, J., Bradshaw, S.M., Akdogan, G., Mpinga, N., **Snyders, C.A**. 2012. A novel energy efficient process for the extraction of platinum group metals through a sequential stage high temperature heap leach process and subsequent recovery and elution using activated carbon. *Biohydrometallurgy '12*, Falmouth, Cornwall, UK, June 18 – 20, 2012

Conferences with no proceedings

Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J., 2012. The elution of platinum group metals from activated carbon. Minproc 2012, The south African mineral beneficiation and metallurgy conference. 2-3 August 2012

Snyders, C.A., Harzenberg, A, Bradshaw, S.M., Akdogan, A, Eksteen, J.J., 2013. The effect of temperature, free cyanide and base metals on the adsorption and elution of Pt, Pd and Au using activated carbon. Minproc 2012, The south African mineral beneficiation and metallurgy conference. 7-8 August 2013

Snyders, C.A., Harzenberg, A, Bradshaw, S.M., Akdogan, A, Eksteen, J.J., 2013. The effect of temperature, free cyanide and base metals on the adsorption and elution of Pt, Pd and Au using activated carbon. 12th conference: International Chemistry Conference Africa. 8 – 12 July 2013.

Snyders, C.A, Bradshaw, S.M, Akdogan, G, Eksteen, J.J., 2013. Modelling the elution of platinum cyanide complexes from activated carbon. Fluent User Group meeting, Stellenbosch, 15 May 2013.

Nomenclature

A	Parameter in Freundlich isotherm expression
B	Parameter in mass flux equiation and modified from the Freundlich isotherm expression
BMs	Base Metals (Copper, Nickel, Cobalt…)
BV	Bed Volume (m^3)
C	liquid phase concentration (mg/L)
C_L	bulk liquid phase concentration (mg/L)
C_2	inertial resistance factor
D	mass diffusivity (m^2/s)
E_{act}	Activation energy (kJ/mol)
F	external force vector (N)
g	gravitational accelaration (m/s^2)
i	specie (subscript)
J	Diffusion flux ($kg/m^2.s$)
k	film transfer coefficient (m/s)
K	mass transfer coefficient ($kg/m^3.s$)
L	length (mm)
Q	concentration of adsorbent on carbon surface (mg/kg)
m	mass (kg)
n	Parameter in Freundlich isotherm expression
N	mass tranfer ($kg/m^3.s$)
p	static pressure (Pa)
PGMs	Precious Group Metals (Platinum, Palladium, Gold)
t	time (s)
T	temperature (°C)
R	Gas constant (J/molK)
V	superficial velocity (m/s)
Y	mass fraction
α	permeability
Ω	computational domain
ε	porosity
ρ	density (kg/m^3)
τ	stress tensor (Pa)
μ	dynamic visocsity ($N.s/m^2$)
∇	del operator which represents the partial derivative of a quantity with respect to all directions in the chosen coordinate system